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Contents

1	Fundamental Principles of Statistical Physics	3
1.1	Review of Topics in Classical Mechanics	3
1.1.1	Hamilton's Equations and Phase Space	3
1.1.2	Phase Flow	6
1.1.3	Liouville's Theorem	7
1.1.4	Poincare's Theorem	8
1.1.5	Necessity of a Statistical Description of Many Particle Systems	10
1.2	Statistical Methods	14
1.2.1	Probability	14
1.2.2	Binomial Distribution	16
1.2.3	Poisson Distribution	17
1.2.4	Averages and Fluctuations	18
1.2.5	Continuous Distributions	20
1.2.6	The Gaussian Distribution and the Central Limit Theorem	21
1.3	Review of Thermodynamics	27
1.3.1	Statistical Description of Large Systems	27
1.3.2	The Equilibrium State	29
1.3.3	Interacting Systems	29
1.3.4	Reversible vs Irreversible Processes	30
1.3.5	Energy, Temperature, and Entropy	31
1.3.6	The Laws of Thermodynamics	33
1.3.7	Thermodynamic Potentials	34
1.3.8	The Simple Example: The Ideal Gas	35
1.4	Statistical Ensembles	36
1.4.1	Gibbsian Ensembles	36
1.4.2	The Microcanonical Ensemble	36
1.4.3	The Canonical Ensemble	37
1.4.4	The Grand Canonical Ensemble	42
1.4.5	The Thermodynamic Limit and the Durham-Gibbs Relation	46
1.4.6	Systems in Magnetic Fields	50
1.5	Quantum Statistical Mechanics	51
1.5.1	The Postulates of Quantum Statistical Mechanics	51
1.5.2	The Density Matrix for Various Ensembles	56

1.5.3	Fermions and Bosons	57
1.5.4	The Fermi-Dirac Distribution	57
1.5.5	The Bose-Einstein Distribution	59
2	Selected Applications	61
2.1	Classical Systems	61
2.1.1	The Classical Monatomic Ideal Gas	61
2.1.2	The Gibbs Paradox	64
2.1.3	The Equipartition Theorem	65
2.1.4	Maxwell's Velocity Distribution – Part I: Canonical Ensembles	68
2.1.5	Maxwell's Velocity Distribution – Part II: Microcanonical Ensemble	71
2.2	The Ideal Fermi Gas	75
2.2.1	Distribution Functions and the Equation of State for Fermions and Bosons	75
2.2.2	The Degenerate Gas	79
2.2.3	The Specific Heat of a Degenerate Electron Gas	80
2.2.4	Pauli Paramagnetism	82
2.3	The Ideal Bose Gas	85
2.3.1	Bose-Einstein Condensates	85
2.3.2	Chemical Potential and Particle Number for $T < T_0$	87
2.3.3	The Specific Heat of an Ideal Bose Gas	89
2.4	Black Body Radiation	91
2.4.1	Planck's Law	91
2.4.2	Discussion of Planck's Law	93
2.5	Relativistic Degenerate Electron Gas	94
3	Introduction to Kinetic Theory	97
3.1	The Boltzmann Equation	97
3.1.1	The Fundamental Question of Kinetic Theory	97
3.1.2	The Collision Operator I: Scattering Out Distribution	99
3.1.3	The Collision Operator II: The “Scattering In” Contribution	100
3.1.4	The Boltzmann Collision Operator	101

Chapter 1

Fundamental Principles of Statistical Physics

1.1 Review of Topics in Classical Mechanics

1.1.1 Hamilton's Equations and Phase Space

Axiom: The state of a system with n degrees of freedom is completely determined by n coordinates $q_i(t)$ and n velocities $\dot{q}_i(t)$ (for $i = 1, \dots, n$)

Lagrangian: The Lagrangian can be written as

$$\mathcal{L}(q, \dot{q}, t)$$

where

$$\dot{q}_i(t) = \frac{dq_i(t)}{dt} \quad \text{and} \quad q(t) = (q_1(t), q_2(t), \dots, q_n(t))$$

Momenta: Similarly, the momenta $p_i(t)$ can be expressed as:

$$p_i(t) = \frac{\partial \mathcal{L}(q, \dot{q}, t)}{\partial \dot{q}_i}$$

Definition 1: The Hamiltonian or Legendre Transformation of \mathcal{L} is given by the function:

$$H(q, p, t) := \sum_{i=1}^n p_i \dot{q}_i - \mathcal{L}(q, \dot{q}, t)$$

Definition 2: The space of $2n$ -tuplets $(q, p) = (q_1, q_2, \dots, q_n, p_1, p_2, \dots, p_n)$ is called the phase space of the system, and is denoted by $\Gamma = \{(q, p)\}$.

Theorem: For every path $q(t)$ in \mathbb{R}^n , there is one and only one path $q(t), p(t)$ in Γ . The path in Γ is determined by Hamilton's Equations or the Canonical Equations.

$$\begin{aligned}\dot{q}_i(t) &= \frac{\partial H(q, p, t)}{\partial p_i} \\ \dot{p}_i(t) &= -\frac{\partial H(q, p, t)}{\partial q_i}\end{aligned}$$

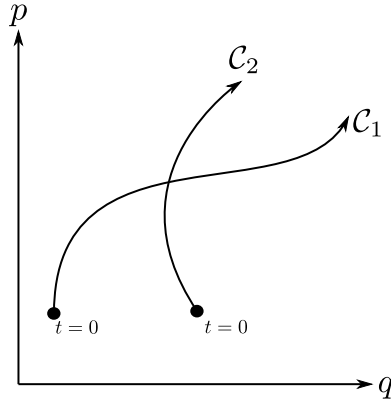
which are equivalent to the Euler-Lagrange equations:

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{q}_i} = \frac{\partial \mathcal{L}}{\partial q_i}$$

Proof: See Phys 505

Remark 1: The Euler-Lagrange equations give n 2nd order ODEs, which is equivalent to the $2n$ 1st order ODEs given by Hamilton's equations.

Remark 2: Given an initial point $(q_0, p_0) \in \Gamma$ with $q_0 = q(t=0)$, $p_0 = p(t=0)$ then this uniquely determines the path $q(t), p(t)$. Thus paths in phase space can not cross.



The above is *NOT* physically possible since $t = 0$ could be chosen to be at the intersection, which would give two different paths with identical initial points.

Remark 3: Using chain rule:

$$\frac{d}{dt} H(q, p, t) = \sum_{i=1}^n \frac{\partial H}{\partial p_i} \dot{p}_i + \sum_{i=1}^n \frac{\partial H}{\partial q_i} \dot{q}_i + \frac{\partial H}{\partial t}$$

Using Hamilton's equations,

$$\begin{aligned} &= \sum_{i=1}^n (\dot{q}_i \dot{p}_i - \dot{p}_i \dot{q}_i) + \frac{\partial H}{\partial t} \\ &= \frac{\partial H}{\partial t} \end{aligned}$$

So if the Hamiltonian has no explicit time dependence, then

$$\frac{d}{dt}H(q, p) = 0$$

which is a 1st integral (conservation law). Thus, as $H(q_0(t), p_0(t)) = E$ which is constant, energy is conserved or autonomous in the problem.

Example: Let's look at a 1-d Harmonic Oscillator

$$n = 1, \quad \mathcal{L} = \frac{1}{2}m\dot{q}^2 - \frac{1}{2}kq^2, \quad \Rightarrow p = \frac{\partial \mathcal{L}}{\partial \dot{q}} = m\dot{q}$$

$$\begin{aligned} H &= p\dot{q} - \mathcal{L} = m\dot{q}^2 - \frac{1}{2}m\dot{q}^2 + \frac{1}{2}kq^2 \\ &= \frac{1}{2}m\dot{q}^2 + \frac{1}{2}kq^2 \\ \Rightarrow H(q, p) &= \frac{p^2}{2m} + \frac{1}{2}kq^2 \end{aligned}$$

The phase space orbit is then

$$\begin{aligned} E &= H(q, p) = \frac{p^2}{2m} + \frac{1}{2}kq^2 \\ \Rightarrow \frac{p^2}{2mE} + \frac{q^2}{2E/k} &= 1 \end{aligned}$$

The canonical equations are:

$$\begin{aligned} \dot{q} &= \frac{\partial H}{\partial p} = \frac{p}{m} \\ \dot{p} &= -\frac{\partial H}{\partial q} = -kq \\ \Rightarrow \ddot{q} &= -\frac{k}{m}q = -\omega^2 q \end{aligned}$$

where $\omega = \sqrt{\frac{k}{m}}$ as per normal.

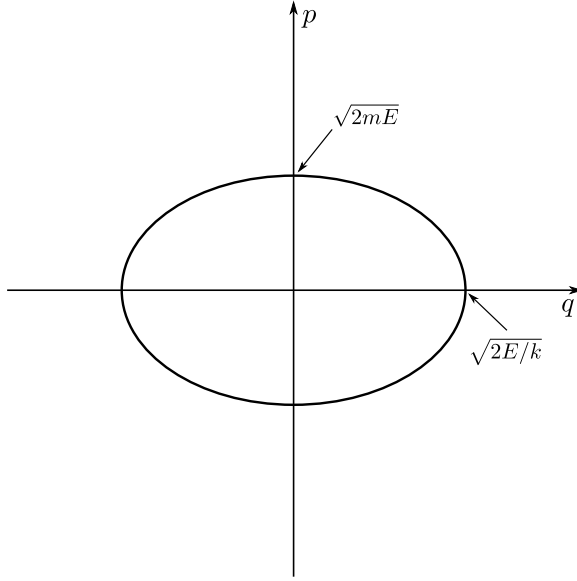


Figure 1.1: Phase space diagram of a simple harmonic oscillator with energy E .

1.1.2 Phase Flow

Let

$$\begin{aligned} (q(t), p(t)) &\equiv z(t) \in \Gamma \\ &= (q_1(t), q_2(t), \dots, q_n(t), p_1(t), p_2(t), \dots, p_n(t)) \end{aligned}$$

Definition 1: The set of mapping $U : \Gamma \rightarrow \Gamma$,

$$U(t, t_0)z(t_0) = z(t)$$

is called phase flow or time-evolution.

Proposition: The time evolution operator, or propagator, $U(t, t_0)$, has the properties:

1. $U(t, t) = \mathbb{I} \quad \forall t$
2. $U(t, t_1)U(t_1, t_0) = U(t, t_0) \quad \forall t, t_0, t_1$
3. $U^{-1}(t, t_0) = U(t_0, t) \quad \forall t, t_0$

Proofs:

- 1.

$$U(t, t)z(t) = z(t) \quad \forall z(t) \in \Gamma$$

$$\therefore U(t, t) = \mathbb{I}$$

2.

$$\begin{aligned}
U(t, t_1)U(t_1, t_0)z(t_0) &= U(t, t_1)z(t_1) = z(t) \\
&= U(t, t_0)z(t_0) \\
\therefore U(t, t_1)U(t_1, t_0) &= U(t, t_0)
\end{aligned}$$

3.

$$\begin{aligned}
U(t_0, t)z(t) &= z(t_0) \\
U^{-1}(t_0, t)U(t_0, t)z(t) &= U^{-1}(t_0, t)z(t_0) \\
z(t) &= U^{-1}(t_0, t)z(t_0) \\
&= U(t, t_0)z(t_0) \\
\therefore U^{-1}(t_0, t) &= U(t, t_0)
\end{aligned}$$

Remark 1: Knowledge of the phase flow is equivalent to knowledge of the solution of the canonical equations.

1.1.3 Liouville's Theorem

Theorem: Let

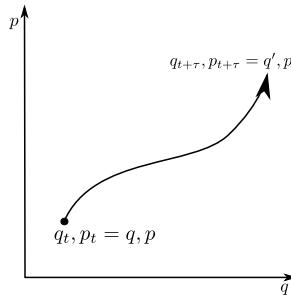
$$d\Gamma = \text{const} \cdot dq_1 dq_2 \cdots dq_n dp_1 dp_2 \cdots dp_n$$

be the element of volume in phase space. Then

$$d\Gamma = \text{constant}$$

In other words, phase flow is volume preserving.

Proof:



Let $q, p = q_t, p_t$ represent q, p at time t , and $q', p' = q_{t+\tau}, p_{t+\tau}$ represent values of q, p at time $t + \tau$. Then we want to show that

$$\int dq_1 dq_2 \cdots dq_n dp_1 dp_2 \cdots dp_n = \int dq'_1 dq'_2 \cdots dq'_n dp'_1 dp'_2 \cdots dp'_n$$

But

$$\int dq'_1 \cdots dq'_n dp'_1 \cdots dp'_n = \int J dq_1 \cdots dq_n dp_1 \cdots dp_n$$

where

$$J = \frac{\partial(q'_1, \dots, q'_n, p'_1, \dots, p'_n)}{\partial(q_1, \dots, q_n, p_1, \dots, p_n)}$$

$$= \begin{vmatrix} \frac{\partial q'_1}{\partial q_1} & \cdots & \frac{\partial q'_1}{\partial q_n} & \frac{\partial q'_1}{\partial p_1} & \cdots & \frac{\partial q'_1}{\partial p_n} \\ \vdots & & & & & \vdots \\ \frac{\partial q'_n}{\partial q_1} & & & & & \vdots \\ \frac{\partial p'_1}{\partial q_1} & & & & & \vdots \\ \vdots & & & & & \vdots \\ \frac{\partial p'_n}{\partial p_1} & \cdots & \cdots & \cdots & \cdots & \frac{\partial p'_n}{\partial p_n} \end{vmatrix}$$

where J is the Jacobian and is the determinant of the above matrix. Proving Liouville's Theorem then boils down to showing that $J=1$. This can be shown using results from Advanced Dynamics:

1. The change in p, q during motion may be regarded as a canonical transformation.
2. Volume in a phase space is invariant under canonical transformations (i.e. $J = 1$ for canonical transformations).

1.1.4 Poincare's Theorem

Theorem: For full mathematical representation and proof, see “Statistical Mechanics” by Huang. A system having a finite energy and confined to a finite volume will, after a sufficiently long time, return to an arbitrarily small neighborhood about almost any given initial state.

Remark 1: Thus, V returns to U after a finite number of steps. This is called the Recurrence Theorem.

Remark 2: Recurrence occurs arbitrarily often and arbitrarily accurately (since U is arbitrary).

Corollary: Let's consider a conservative mechanical system at some initial time to be in a state given by a point in phase space, $z_0 \in \Gamma$. Then the system will come arbitrarily close to z_0 again in finite time.

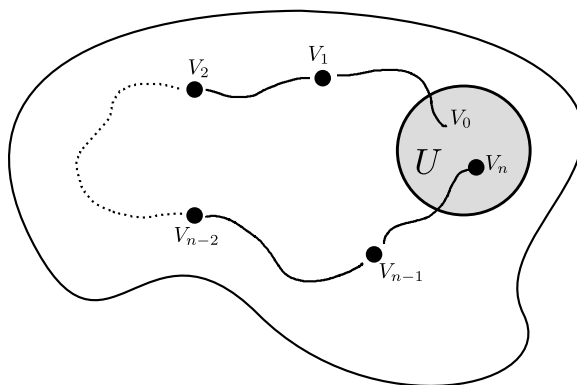
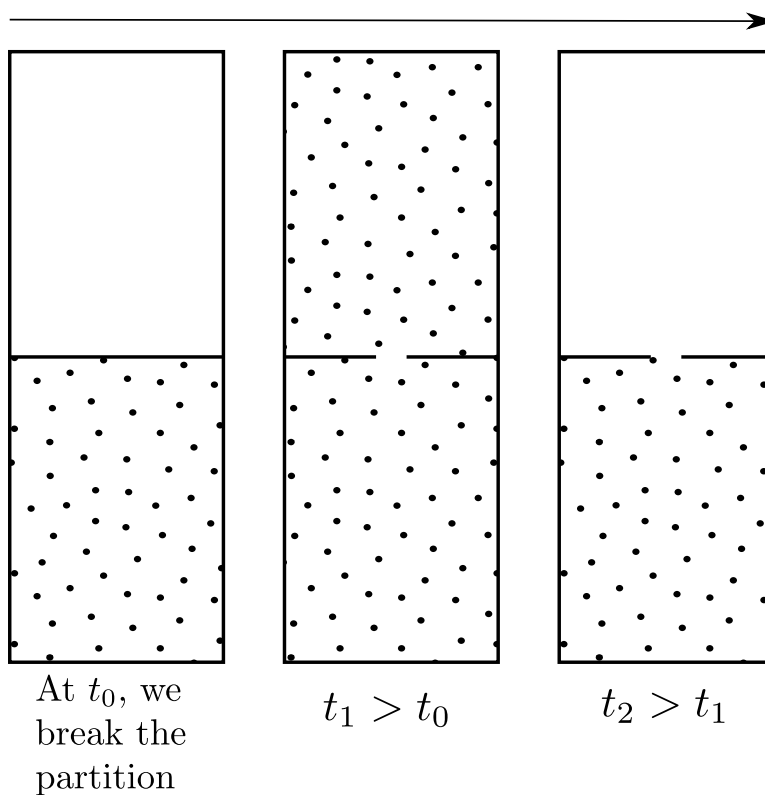


Figure 1.2: Graphical representation of Poincaré's Theorem. The outer shape is some bounded region in \mathbb{R}^2 (for example), V_0 is the initial state of the system, U is a neighborhood around V_0 , and the lines mark the path of the system through time.

Example: Gas in a partitioned container



So, according to Poincaré, at finite t_2 , all the gas will go back into the single side of the container!

Problem: This is *NOT* what we observe!

Solution:

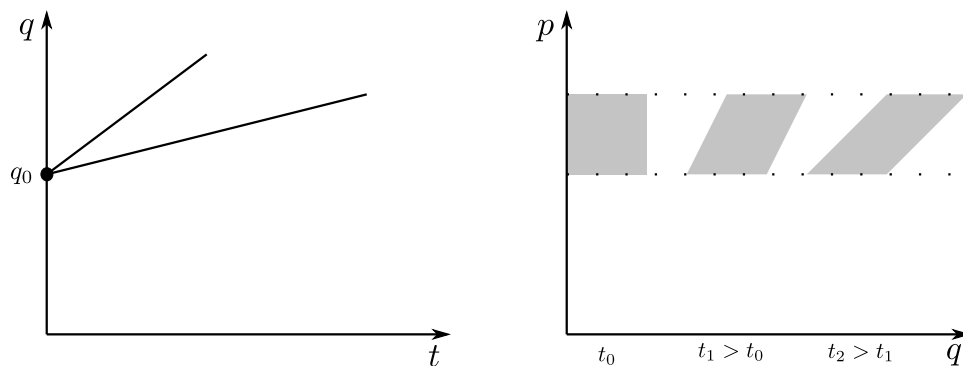
1. The “finite” time is ridiculously long for large systems.
2. Anything else? Yes! According to Boltzmann, this state would represent a “fluctuation from equilibrium and is thus still consistent with statistical description.

1.1.5 Necessity of a Statistical Description of Many Particle Systems

Example 1: Here we’ll look at a free particle in 1 dimension (which is thus not bounded).

$$p(t) = p_0$$

$$q(t) = q_0 + \left(\frac{p_0}{m}\right) t$$



By Liouville’s theorem, the volume in phase space is conserved. But it never returns to its initial state since the region is not bounded (and thus Poincaré does *not* hold).

Example 2: Now we’ll look at a particle in a 1 dimensional potential well (so the system is now bounded).

$$p(t) = \pm p_0$$

$$q(t) = q_0 + \left(\frac{p_0}{m}\right) t + \text{inverted motion}$$

As seen in the following figure, notice that p is not continuous, and thus the region becomes disconnected. Thus we should modify the theory to allow for disconnected volumes. Also note that, as $t \rightarrow \infty$, the disconnected parts become thinner and thinner, which leads to spaghetti structure.

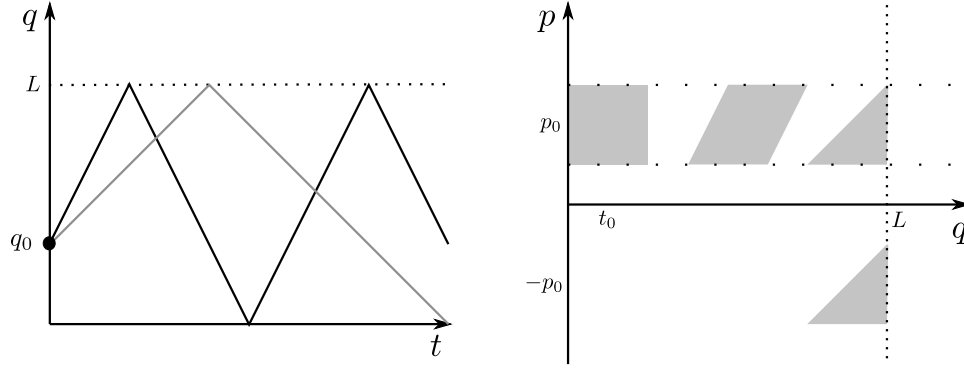
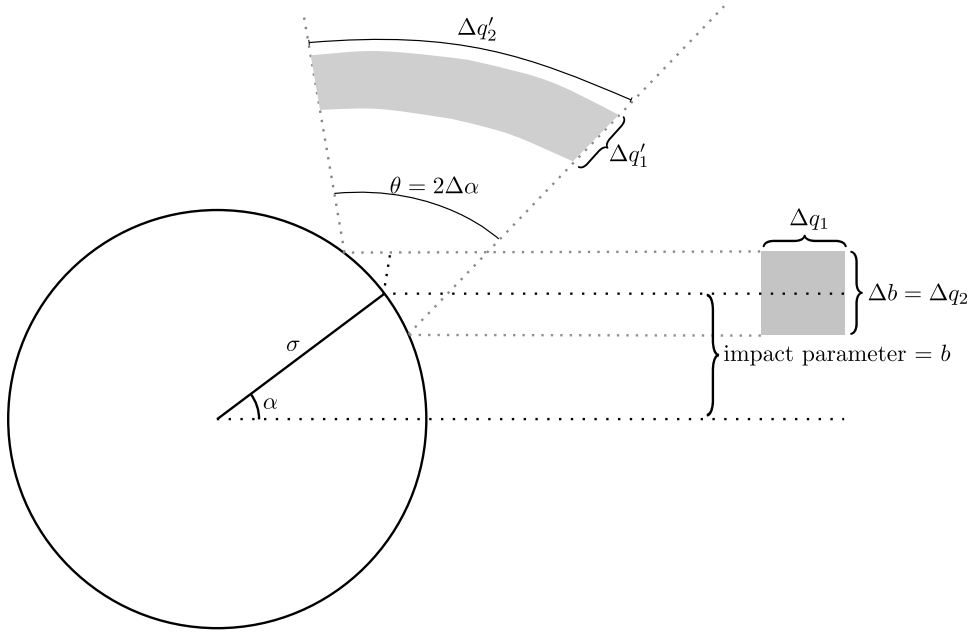


Figure 1.3: Spatial and phase space plots for a particle trapped in a potential well.

Example 3: For the final example, we'll look at a particle scattered by a hard sphere in 3 dimensions.



We know that

$$\sin \alpha = \frac{b}{\sigma}, \quad \Delta q_1 = \Delta q'_1, \quad \Delta q'_2 > \Delta q_2 = \Delta b$$

So the q contribution to phase space volume increases due to scattering. This means that, in order to keep the phase space volume invariant, the momentum contribution must decrease. Let

$$\alpha \ll 1 \quad \Rightarrow \quad \Delta \alpha = \frac{\Delta b}{\sigma} = \frac{\Delta q_2}{\sigma}$$

and let the mean-free path l be

$$l \gg \sigma.$$

Therefore, the new spacial volume after 1 collision would be:

$$\begin{aligned} V' &= \Delta q'_1 \cdot l \cdot 2\Delta\alpha \quad (\text{in 2D}) \\ &= \Delta q'_1 \cdot 2l \cdot \frac{\Delta q_2}{\sigma} \\ &= V \cdot \frac{2l}{\sigma} \end{aligned}$$

where $V = \text{the initial volume} = \Delta q_1 \Delta q_2$. In d -dimensions then:

$$V' \sim V \left(\frac{2l}{\sigma} \right)^{d-1}$$

Now Liouville's theorem tells us that the momentum-space contribution to the phase space volume must decrease by a factor of $\left(\frac{\sigma}{2l}\right)^{(d-1)N}$ after N collisions.

Problem - “The Butterfly Effect”: After N collisions, a simple volume in phase space has been transformed into spaghetti in momentum space with typical dimensions given by

$$\frac{\Delta p_N}{p_N} \sim \left(\frac{\sigma}{2l} \right)^{(d-1)N}$$

Example: Consider a classical gas of hard spheres of radius σ and number density n .

$$l \sim (n\sigma^2)^{-1}$$

$$\begin{aligned} \Rightarrow \frac{\sigma}{l} &\sim n\sigma^3 \equiv n^* \quad \leftarrow \text{dimensionless density} \\ &\approx 10^{-3} \text{ for typical gas} \end{aligned}$$

For 3 dimensions and 3 collisions ($D = 3, N = 3$):

$$\frac{\Delta p_N}{p_N} \sim (10^{-3})^{2 \cdot 3} = 10^{-18}$$

So we would have to keep this accuracy to track the particles accurately. Thus, after a few collisions, a ridiculous level of accuracy is needed to maintain the spaghetti structure.

Remark 1: Consider a real experiment, where we will be looking at the effect of gravitational attraction between an external butterfly and our system.

$$\frac{F}{m} = \frac{GM}{r^2} = 7 \times 10^{-11} \frac{M}{r^2}$$

The momentum uncertainty due to F is:

$$\Delta p = F\tau$$

where τ is the mean free time between particles.

$$\tau = \frac{l}{v}$$

$$\Rightarrow \frac{\Delta p}{p} \sim \left(\frac{F\tau}{mv} \right) = \left(\frac{F}{m} \right) \left(\frac{\tau}{v} \right)$$

For a classical gas: $v = 10^3$ m/s, $\tau \sim 10^{-9}$ s.

$$\Rightarrow \frac{\Delta p}{p} \sim 10^{-22} \frac{M}{r^2}$$

- If the butterfly is $m = 1$ gram and $r = 100$ m.

$$\frac{\Delta p}{p} \sim 10^{-22-7} = 10^{-29}$$

We know spaghetti structure is destroyed after

$$\frac{\Delta p_N}{p_N} \sim \left(\frac{\sigma}{2l} \right)^{(d-1)N}$$

Setting $\frac{\Delta p}{p} = \frac{\Delta p_N}{p_N}$ and solving for N yields:

$$N = 5$$

Thus, after only 5 collisions, the butterfly outside will affect the spaghetti structure of the system inside.

- If instead the butterfly (still $m = 1$ gram) is on the star Sirius ($r = 8.5$ light-years or 8×10^{16} m):

$$\frac{\Delta p}{p} = 10^{-22-35} = 10^{-57}$$

$$\Rightarrow N = 9 \text{ collisions (which takes about } 100\mu\text{s)}$$

So again, we are screwed up even by butterflies on Sirius! Now, in order for the “picture” to reappear in the recurrence relation, the spaghetti structure must be conserved. Thus, uncontrollable forces in the microscopic world destroy spaghetti structure.

Remark 2: If, instead, we were to consider a computer experiment, we would be free of outside effects, but would instead introduce uncontrollable perturbations in the form of rounding errors.

Conclusions:

1. Microscopically deterministic descriptions of N-particle systems over macroscopic times (with time reversibility, Poincare's theorem, etc) are impossible due to uncontrollable weak forces.
2. In experience, time average of macroscopic quantities are independent of the instabilities in phase-space structure.
3. We must develop a statistical, rather than deterministic, description of many particle systems.

Remark 3: According to Boltzmann, the recurrence of states are fluctuations, which are certain to occur if you wait long enough. Thus, recurrence relations are completely consistent with a statistical viewpoint.

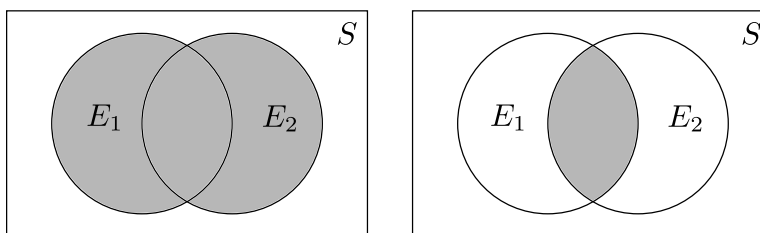
1.2 Statistical Methods

1.2.1 Probability

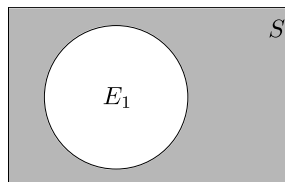
Definition 1: Consider a set $S \neq \emptyset$ which is the set of all possible outcomes of an experiment. This is called the sample set.

Definition 2: Let E be any subset of S . E is called an event and satisfies:

1. $E \subset S \forall E$
2. $\forall E_1, E_2 \subset S, (E_1 \cup E_2) \subset S \wedge (E_1 \cap E_2) \subset S$
 “For events E_1 and E_2 that are both possible, then E_1 or E_2 must also be possible, as well as E_1 and E_2 being possible.”



3. $E \subset S, S/E \subset S$



Definition 3: Each event is assigned a statistical weight or probability $P(E)$ so that:

1. $0 \leq P(E) \leq 1 \forall E$
2. $P(E_1 \cup E_2) = P(E_1) + P(E_2) - P(E_1 \cap E_2)$
3. $P(S) = 1, \quad P(\emptyset) = 0$

Example: We will consider rolling a fair die:

$$S = \{1, 2, 3, 4, 5, 6\}$$

$$\text{Any } E \subset S \text{ is an event } \begin{cases} E = 1, \\ E = \{1, 3, 5\}, \\ \text{etc} \end{cases}$$

$$P(E) = \frac{(\text{number of elements in } E)}{6}$$

Proposition: The probability of mutually exclusive events equals the sum of the individual probabilities.

Proof: If you have mutually exclusive events, then $E_1 \cap E_2 = \emptyset$. Thus

$$\begin{aligned} P(E_1 \cup E_2) &= P(E_1) + P(E_2) - \underbrace{P(E_1 \cap E_2)}_0 \\ &= P(E_1) + P(E_2) \end{aligned}$$

Definition 4: Let E_1 and E_2 be events. The joint probability of E_1 and E_2 is defined as

$$P(E_1, E_2) = P(E_1 \cap E_2)$$

Definition 5: If E_1 and E_2 are statistically independent, then

$$P(E_1, E_2) = P(E_1)P(E_2)$$

Example: Probability of getting either a 1 or a 6 in rolling 1 die once? The events are mutually exclusive, so

$$P(1 \cup 6) = P(1) + P(6) = \frac{1}{6} + \frac{1}{6} = \frac{1}{3}$$

Example: Probability of getting a 1 *and* a 6 when rolling 2 die once?

$$P(1, 6) + P(6, 1) = \left(\frac{1}{6}\right) \left(\frac{1}{6}\right) + \left(\frac{1}{6}\right) \left(\frac{1}{6}\right) = \frac{1}{18}$$

Also

$$S = \{(1, 1), (1, 2), \dots, (1, 6), \\ (2, 1), (2, 2), \dots \\ \vdots \\ (6, 1), (6, 2), \dots, (6, 6)\}$$

All possible events are equally likely. Odds are 2 out of 36 possible

$$\frac{2}{36} = \frac{1}{18}$$

Remark 1: It is non-trivial to determine whether events are statistically independent!

Definition 6: A probability distribution is the set of probabilities P_i so that

$$\sum_i P_i = 1$$

A quantity given by a probability distribution is called a random variable.

1.2.2 Binomial Distribution

Theorem: Let there be S independent attempts, and let the probability of a certain event in each attempt be p . The probability of an event occurring n times is:

$$\rho_b(n, S) = \binom{S}{n} p^n (1-p)^{S-n} \quad (\star)$$

where

$$\binom{S}{n} = \frac{S!}{n!(S-n)!}$$

Proof: The number of ways to partition n events and $(S-n)$ non-events (out of S total attempts) is

$$\binom{S}{n}$$

And so

$$\rho_b(n, S) = \binom{S}{n} \rho^*(n, S)$$

where ρ^* is the probability of realizing a particular partition. The probability for an event is p ; thus the probability for a non-event is $(1-p)$. Thus

$$\rho^* = p^n (1-p)^{S-n}$$

Remark 1: ρ_b is called the binomial distribution.

Remark 2:

$$\sum_{n=0}^S \rho_b(n, S) = \sum_{n=0}^S \binom{S}{n} p^n (1-p)^{S-n}$$

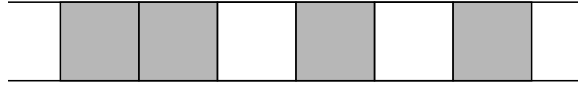
Recall from the binomial theorem that

$$(x+y)^n = \sum_{k=0}^n \binom{n}{k} x^k y^{n-k}$$

Thus

$$\begin{aligned} \sum_{n=0}^S \rho_b(n, S) &= (p + 1 - p)^S \\ &= 1^S \\ &= 1 \end{aligned}$$

Remark 3: Looking at an equivalent type problem, consider sites or boxes occupied with either 0 or 1 indistinguishable objects. Picking S sites, what is the probability of



finding n objects on the S sites, where on average $n = m$?

$$\begin{aligned} \rho_b(n, S; m) &= \binom{S}{n} \left(\frac{m}{S}\right)^n \left(1 - \frac{m}{S}\right)^{S-n} \\ &= \frac{S!}{n!(S-n)!} \frac{m^n (S-m)^{S-n}}{S^S} \end{aligned}$$

1.2.3 Poisson Distribution

Proposition: A continuum of positions can be occupied by indistinguishable objects. Let the average number of objects in any sub-region by m . Then the probability of finding n objects in that sub-region is:

$$\rho_p(n; m) = \frac{1}{n!} m^n e^{-m}$$

This is the Poisson Distribution.

Example: Consider a Geiger counter subject to constant radio activity. The probability of n clicks/sec if, on average, there are m clicks/sec, is given by a Poisson distribution. (Let the number of boxes go to infinity while keeping the density constant.)

Lemma - Stirlings Formula: For $n \gg 1$,

$$n! = \sqrt{2\pi n} n^n e^{-n} \left[1 + \mathcal{O}\left(\frac{1}{n}\right)\right]$$

This can also be written:

$$\ln n! = n \ln n - n + \frac{1}{2} \ln(2\pi n) + \mathcal{O}\left(\frac{1}{n}\right)$$

Proof: See Reif Appendix A6

Proof of Proposition: By §1.2.2.R3,

$$\rho_b(n, S; m) = \frac{S!}{n!(S-n)!} \frac{m^n (S-m)^{S-n}}{S^S}$$

Let $S \rightarrow \infty$ while keeping n, m fixed. Then

$$\rho_p = \rho_b(n, S \rightarrow \infty; m)$$

Consider

$$\begin{aligned} \ln \left[\frac{n! \rho_b}{m^n} \right] &= \lim_{S \rightarrow \infty} \ln \left[\frac{S!}{(S-n)!} \frac{(S-m)^{S-n}}{S^S} \right] \\ &= \lim_{S \rightarrow \infty} [\ln S! - \ln(S-n)! + (S-n) \ln(S-m) - S \ln S] \\ &= \lim_{S \rightarrow \infty} \left[S \ln S - S + \frac{1}{2} \ln(2\pi S) + \mathcal{O}\left(\frac{1}{S}\right) - (S-n) \ln(S-n) \right. \\ &\quad \left. + \frac{1}{2} \ln(2\pi(S-n)) + \mathcal{O}\left(\frac{1}{S-n}\right) + (S-n) \ln(S-m) - S \ln S \right] \\ &= \lim_{S \rightarrow \infty} \left[\frac{1}{2} \ln(2\pi) + \frac{1}{2} \ln(S) - S \ln S - S \ln\left(1 - \frac{n}{S}\right) + n \ln S + n \ln\left(1 - \frac{n}{S}\right) \right. \\ &\quad \left. - n - \frac{1}{2} \ln(2\pi) - \frac{1}{2} \ln S - \frac{1}{2} \ln\left(1 - \frac{n}{S}\right) + S \ln S + S \ln\left(1 - \frac{m}{S}\right) \right. \\ &\quad \left. - n \ln S - n \ln\left(1 - \frac{m}{S}\right) + \mathcal{O}\left(\frac{1}{S}\right) \right] \\ &= \lim_{S \rightarrow \infty} \left[n - n - m + \mathcal{O}\left(\frac{1}{S}\right) \right] \\ &= -m \end{aligned}$$

$$\Rightarrow \rho_p = \frac{1}{n!} m^n e^{-m}$$

1.2.4 Averages and Fluctuations

Let $\rho(n)$ be a probability distribution for some event to occur n times. Let $f(n)$ be some function of n .

Definition 1:

$$\langle f(n) \rangle_\rho := \sum_n f(n) \rho(n)$$

is called the average or mean of $f(n)$.

Remark 1: $\langle f(n) \rangle$ is independent of n .

Remark 2: Averages are defined with respect to a particular distribution.

Remark 3: Choose $f(n) = n^m$:

$$\langle n^m \rangle = \sum_n n^m \rho(n)$$

This is called the m^{th} moment of the distribution of $\rho(n)$.

Remark 4: The zeroth moment is

$$\langle n^0 \rangle = \langle 1 \rangle = \sum_n \rho(n) = 1 \quad \text{by normalization}$$

Example: The first moment of $\rho_p(n; m)$:

$$\begin{aligned} \langle n \rangle_{\rho_p} &= \sum_{n=0}^{\infty} n \frac{1}{n!} m^n e^{-m} \\ &= \sum_{n=1}^{\infty} \frac{1}{(n-1)!} m^n e^{-m} \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} m^{n+1} e^{-m} \\ &= m e^{-m} \underbrace{\sum_{n=0}^{\infty} \frac{1}{n!} m^n}_{e^m} \\ &= m \end{aligned}$$

which agrees with the definition of the Poisson distribution! Yay!

Definition 2:

- $\langle (\Delta n)^2 \rangle_\rho = \langle (n - \langle n \rangle)^2 \rangle_\rho$ is called the mean squared deviation, the variance, or the 2nd moment about the mean of the distribution.

- $(\Delta n) := \langle (\Delta n)^2 \rangle^{1/2}$ is called the root mean squared (RMS) deviation or the standard deviation. Common notation has $\sigma = \Delta n$ and it gives us a measure of the width of the distribution.
- $\frac{\Delta n}{\langle n \rangle}$ is called the relative fluctuation.

Example: The 2nd moment of $\rho_p(n; m)$ is:

$$\begin{aligned}
 \langle n^2 \rangle_{\rho_p} &= \sum_{n=0}^{\infty} n^2 \frac{1}{n!} m^n e^{-m} \\
 &= m e^{-m} \sum_{n=0}^{\infty} \frac{(n+1)}{n!} m^n \\
 &= m e^{-m} (m e^m + e^m) \\
 &= m^2 + m
 \end{aligned}$$

$$\begin{aligned}
 \Delta n &= \langle (n - \langle n \rangle)^2 \rangle_{\rho_p}^{1/2} = \left(\langle n^2 \rangle - \langle n \rangle^2 \right)^{1/2} \\
 &= (m^2 + m - m^2)^{1/2} \\
 &= m^{1/2}
 \end{aligned}$$

Remark 5: For large numbers of events, the size of the expected deviations from the mean, measured in units from the mean, goes to 0. In other words, the distribution becomes sharply peaked. This is known as the Law of Large Numbers.

1.2.5 Continuous Distributions

Definition 1: Let x be a continuous random variable, and let $\rho(x)$ be the probability density that the variable has the value x . Then $\rho(x) dx$ is the probability that the value will lie in the interval between x and $x + dx$. Let $\int \rho(x) dx = 1$. Then $\rho(x)$ is the (continuous) probability distribution function.

Definition 2: Moments, etc are defined by generalizations of §1.2.4.

$$\begin{aligned}
 \langle x^n \rangle &= \int x^n \rho(x) dx && \text{nth moment} \\
 \sigma \equiv \Delta x &:= \left(\langle x^2 \rangle - \langle x \rangle^2 \right)^{1/2} && \text{RMS Deviation}
 \end{aligned}$$

Example: A factory produces resistors with a nominal resistivity of R . Actual resistivities will be distributed according to some distribution function $\rho(R)$.

Remark 1: We can always return to discrete values of the random variable by considering δ -function distributions.

Example: Suppose x can take on only integer values between 1 and N with equal probability.

$$\Rightarrow \rho(x) = \frac{1}{N} \sum_{n=1}^N \delta(x - n)$$

is a continuous distribution function describing the above situation.

$$\int \rho(x) dx = 1$$

$$\begin{aligned} \int x \rho(x) dx &= \frac{1}{N} \sum_{n=1}^N \int x \delta(x - n) dx \\ &= \frac{1}{N} \sum_{n=1}^N n \\ &= \frac{1}{N} \left(\frac{1}{2} N(N+1) \right) \\ &= \frac{1}{2} (N+1) \end{aligned}$$

1.2.6 The Gaussian Distribution and the Central Limit Theorem

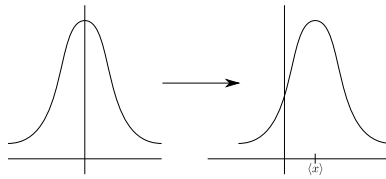
Definition 1: Let x be a random variable with distribution

$$\rho_G(x) = \frac{1}{\sigma \sqrt{2\pi}} e^{-x^2/2\sigma^2}$$

Then $\rho_G(x)$ is called a Gaussian or normal distribution.

Remark 1: $\langle x \rangle = 0$. This can be trivially generalized by making the following substitution

$$x \rightarrow x - \langle x \rangle$$



Remark 2: σ is the standard deviation of ρ_G :

$$\langle x^2 \rangle = \frac{1}{\sigma\sqrt{2\pi}} \int x^2 e^{-x^2/2\sigma^2} dx$$

Scaling $x \rightarrow \sqrt{2}\sigma x$

$$\begin{aligned} &= \frac{1}{\sigma\sqrt{2\pi}} 2\sigma^2 \sqrt{2}\sigma \underbrace{\int x^2 e^{-x^2} dx}_{\frac{1}{2}\sqrt{\pi}} \\ &= \sigma^2 \end{aligned}$$

Lemma: The moments of the Gaussian distribution are:

$$\langle x^n \rangle = \begin{cases} 0 & \text{if } n = \text{even} \\ \frac{n! \sigma^n}{2^{n/2} (\frac{n}{2})!} & \text{if } n = \text{odd} \end{cases}$$

Proof:

$$\langle x^{2n+1} \rangle = 0 \quad \text{by symmetry}$$

$$\begin{aligned} \langle x^{2n} \rangle &= \frac{1}{\sigma\sqrt{1\pi}} \int_{-\infty}^{\infty} x^{2n} e^{-x^2/2\sigma^2} dx \quad x \rightarrow \sqrt{2}\sigma x \\ &= \frac{1}{\sigma\sqrt{2\pi}} (\sqrt{2}\sigma)^{2n+1} 2 \int_0^{\infty} x^{2n} e^{-x^2} dx \end{aligned}$$

Now, looking at

$$\int_0^{\infty} x^{2n} e^{-x^2} dx$$

recall that

$$\Gamma(z) = \int_0^{\infty} t^{z-1} e^{-t} dt$$

Letting $t = x^2$, we see that

$$\begin{aligned} \Rightarrow \int_0^{\infty} x^{2n} e^{-x^2} dx &= \int_0^{\infty} \frac{1}{2} t^{n-1} e^{-t} dt \\ &= \int_0^{\infty} \frac{1}{2} t^{n+\frac{1}{2}-1} e^{-t} dt \\ &= \frac{1}{2} \Gamma\left(n + \frac{1}{2}\right) \end{aligned}$$

$$\begin{aligned} \Rightarrow \langle x^{2n} \rangle &= \frac{1}{\sigma\sqrt{2\pi}} (\sqrt{2}\sigma)^{2n+1} \cdot 2 \cdot \frac{1}{2} \Gamma\left(n + \frac{1}{2}\right) \\ &= \frac{1}{\sqrt{\pi}} (2\sigma^2)^n \Gamma\left(n + \frac{1}{2}\right) \end{aligned}$$

$$\begin{aligned}
\text{Since } \Gamma(z)\Gamma(z + \tfrac{1}{2}) &= \frac{\sqrt{\pi}\Gamma(2z)}{2^{2z-1}} \\
&= \frac{(2\sigma^2)^n}{\sqrt{\pi}} \frac{\sqrt{\pi}\Gamma(2n)}{\Gamma(n)2^{2n-1}} \\
&= \frac{2^n \sigma^{2n} (2n-1)!}{2^{2n-1} (n-1)!} \\
&= 2 \left(\frac{2}{4}\right)^n \sigma^{2n} \frac{(2n)!}{2n} \frac{n}{n!} \\
&= \frac{\sigma^{2n} (2n)!}{2^n n!}
\end{aligned}$$

Definition 2: The characteristic function $f(x)$ of a distribution $\rho(x)$ is defined as:

$$f(k) = \left\langle e^{-ikx} \right\rangle_{\rho} = \int e^{-ikx} \rho(x) dx$$

(ie. the fourier transform of $\rho(x)$)

Lemma: For a gaussian distribution

$$f(k) = e^{-k^2 \sigma^2 / 2}, \quad \rho(x) = \int \frac{1}{2\pi} f(k) e^{ikx} dk$$

(since the fourier transform of a gaussian is a gaussian).

Proof:

$$\begin{aligned}
f(k) &= \left\langle e^{-ikx} \right\rangle_{\rho} \\
&= \sum_{n=0}^{\infty} \left\langle \frac{(-ikx)^n}{n!} \right\rangle_{\rho} \\
&= \sum_{n=0}^{\infty} \left\langle \frac{(-ikx)^{2n}}{(2n)!} \right\rangle_{\rho} \\
&= \sum_{n=0}^{\infty} \frac{(-1)^n k^{2n}}{(2n)!} \langle x^{2n} \rangle \\
&= \sum_{n=0}^{\infty} \frac{(-1)^n k^{2n}}{(2n)!} \frac{(2n)! \sigma^{2n}}{2^n n!} \\
&= \sum_{n=0}^{\infty} \frac{\left(\frac{-k^2 \sigma^2}{2}\right)^n}{n!} \\
&= e^{-k^2 \sigma^2 / 2}
\end{aligned}$$

$$\begin{aligned}
\int \frac{1}{2\pi} f(k) e^{ikx} dk &= \int e^{-k^2\sigma^2/2} e^{ikx} \frac{dk}{2\pi} \\
&= \frac{1}{2\pi} \int \exp \left[\frac{-\sigma^2}{2} \left(k^2 - \frac{2i}{\sigma^2} kx - \frac{x^2}{\sigma^4} + \frac{x^2}{\sigma^4} \right) \right] dk \\
&= \frac{1}{2\pi} e^{-x^2/2\sigma^2} \int \exp \left[-\frac{\sigma^2}{2} \left(k - \frac{ix}{\sigma^2} \right)^2 \right] dk \\
&= e^{-x^2/2\sigma^2} \int \exp \left(-\frac{\sigma^2}{2} k^2 \right) \frac{dk}{2\pi} \\
&= e^{-x^2/2\sigma^2} \frac{1}{2\pi} \frac{\sqrt{2}}{\sigma} \int e^{-k^2} dk \\
&= \frac{1}{\sqrt{2\pi}} \frac{1}{\sigma} e^{-x^2/2\sigma^2} \\
&= \rho(k)_G
\end{aligned}$$

Theorem: Central Limit Theorem: Let x_i ($i = 1, \dots, N$) be N independent random variables with $\langle x_i \rangle = 0 \quad \forall i$ and $\langle x_i^2 \rangle < \infty \quad \forall i$. Also let $y = \frac{1}{N} \sum_{i=1}^N x_i$ be the arithmetic mean (ie. the average with respect to a flat distribution) of x_i . Then, for $N \rightarrow \infty$, y is gaussian distributed with a standard deviation of $\sigma \sim \frac{1}{\sqrt{N}}$.

$$\rho(y) = \frac{1}{\sigma\sqrt{2\pi}} e^{-y^2/2\sigma^2}$$

with

$$\sigma^2 = \frac{1}{N^2} \sum_{i=1}^N \langle x_i^2 \rangle$$

Remark 3: According to the law of large numbers, for large numbers of events the distribution is sharply peaked about its mean. And the CLT (Central Limit Theorem) tells us that the distribution in that limit is gaussian.

Remark 4: This holds irrespective of what the distribution of x is, so long as $\langle x_i^2 \rangle < \infty$.

Remark 5: Generalizing to $\langle x_i \rangle \neq 0$:

$$\rho(y) = \frac{1}{\sigma\sqrt{2\pi}} \exp \left[- (y - \langle y \rangle)^2 / 2\sigma^2 \right]$$

with

$$\sigma^2 = \frac{1}{N^2} \sum_{i=1}^N \langle (x_i - \langle x_i \rangle)^2 \rangle$$

Simple Proof of Theorem:

$$\begin{aligned}
\langle e^{-iky} \rangle &= \left\langle \exp \left(-ik \frac{1}{N} \sum_{i=1}^N x_i \right) \right\rangle \\
&= \left\langle \prod_{i=1}^N e^{-ikx_i/N} \right\rangle \\
&= \prod_{i=1}^N \langle e^{-ikx_i/N} \rangle \quad \text{since independent } x_i\text{'s} \\
&= \exp \left[\ln \left(\prod_{i=1}^N \langle e^{-ikx_i/N} \rangle \right) \right] \\
&= \exp \left[\sum_{i=1}^N \ln \langle e^{-ikx_i/N} \rangle \right] \\
&:= \exp \left[\sum_{i=1}^N A_i \left(\frac{k}{N} \right) \right]
\end{aligned}$$

where

$$A_i(p) = \ln \langle e^{-ipk_i} \rangle$$

Now, for $N \rightarrow \infty$, we expand:

$$\begin{aligned}
A_i \left(\frac{k}{N} \right) &= \ln \left\langle 1 + \frac{ik}{N} x_i - \frac{1}{2} \left(\frac{k}{N} \right)^2 x_i^2 \right\rangle \\
&= \ln \left[1 - \frac{1}{2} \left(\frac{k}{N} \right)^2 \langle x_i \rangle^2 + \dots \right] \\
&= \frac{-k^2}{2N^2} \langle x_i^2 \rangle + \mathcal{O}(\frac{1}{N^3}) \\
\Rightarrow \langle e^{-iky} \rangle &= \exp \left[- \sum_{i=1}^N \frac{k^2}{2N^2} \langle x_i \rangle^2 \left[1 + \mathcal{O}(\frac{1}{N}) \right] \right] \\
&= e^{-k^2 \sigma^2 / 2}
\end{aligned}$$

where

$$\sigma^2 = \frac{1}{N^2} \sum_{i=1}^N \langle x_i^2 \rangle$$

By the Lemma then, $\rho(y)$ is gaussian where:

$$\rho(y) = \frac{\sigma \sqrt{2\pi}}{e^{-y^2/2\sigma^2}} \quad \text{with} \quad \sigma^2 = \frac{1}{N^2} \sum_{i=1}^N \langle x_i^2 \rangle$$

Finally, let

$$\chi = \sup \{ \langle x_i^2 \rangle \}$$

Then

$$\begin{aligned} \sigma^2 &\leq \frac{1}{N^2} \chi N = \frac{\chi}{N} \\ \Rightarrow \sigma &\sim \frac{1}{\sqrt{N}} \end{aligned}$$

Example: By §2.2, we have a binomial situation of S total events with:

$$\begin{aligned} n_i &= \begin{cases} 1 & \text{with probability } p \\ 0 & \text{with probability } (1-p) \end{cases} \\ \Rightarrow \rho(n_i) &= p\delta(n_i - 1) + (1-p)\delta(n_i) \end{aligned}$$

Consider

$$n = \sum_{i=1}^S n_i$$

so that n obeys a binomial distribution. Then

$$\rho(n) = \rho_b(n; S) = \binom{S}{n} p^n (1-p)^{S-n}$$

$$\langle n_i \rangle = \frac{1}{S} \sum_{i=1}^S n_i = p = \frac{n}{S}$$

$$\langle n_i^2 \rangle = \frac{1}{S} \sum_{i=1}^S n_i^2 = p \quad \text{since } n_i = \{0, 1\} \Rightarrow n_i^2 = n_i$$

CLT says $(\frac{n}{S})$ is gaussian distributed as S gets large:

$$\rho\left(\frac{n}{S}\right) = \frac{1}{\tilde{\sigma}\sqrt{2\pi}} \exp\left[-\frac{\left(\frac{n}{S} - \langle \frac{n}{S} \rangle\right)^2}{2\tilde{\sigma}^2}\right]$$

where

$$\begin{aligned} \tilde{\sigma}^2 &= \frac{1}{S^2} \sum_{i=1}^S \left(\langle n_i^2 \rangle - \langle n_i \rangle^2 \right) \\ &= \frac{1}{S^2} (Sp - Sp^2) \\ &= \frac{p}{S} (1-p) \\ &:= \frac{\sigma}{S} \\ \Rightarrow \sigma^2 &= p(1-p) \end{aligned}$$

Changing variables:

$$\rho\left(\frac{n}{S}\right) d\left(\frac{n}{S}\right) = \rho(n) dn$$

$$\begin{aligned} \Rightarrow \rho(n) &= \frac{1}{S} \rho\left(\frac{n}{S}\right) = \frac{1}{\tilde{\sigma}\sqrt{2\pi}S} \exp\left[\frac{-(n - \langle n \rangle)^2}{2S^2\tilde{\sigma}^2}\right] \\ &= \frac{1}{\sigma\sqrt{2\pi}S} \exp\left[\frac{-(n - \langle n \rangle)^2}{2S\sigma^2}\right] \end{aligned}$$

Let $\tilde{\sigma} = \sqrt{S}\sigma$:

$$= \frac{1}{\tilde{\sigma}\sqrt{2\pi}} \exp\left[\frac{-(n - \langle n \rangle)^2}{2\tilde{\sigma}^2}\right]$$

$$\tilde{\sigma}^2 = S\sigma^2 = Sp(1-p)$$

And we see that n is indeed gaussian distributed.

1.3 Review of Thermodynamics

1.3.1 Statistical Description of Large Systems

Problem: From §1.1.5, we saw that for macroscopic systems ($\sim 10^{23}$ particles), we can not solve deterministically by solving the equations of motion, even if this were desirable.

Solution: Distinguish between a system's microstate, which is classically given by a point $\gamma \in \Gamma$ (Quantum mechanically, this is a stationary state given by a many body wavefunction $\Psi(x_1, x_2, \dots, x_{10^{23}})$) and its macrostate, which is specified by values of certain macroscopic parameters (ie. energy, temperature, pressure, etc.).

Definition 1:

- For a given energy E , the number of microstates whose energy is $\leq E$ is denoted by $\Omega(E)$ and is called the integrated density of states or the total number of states.
- The density of states is

$$\omega(E) := \frac{d\Omega(E)}{dE}$$

which is the number of microstates per energy interval at a given point in energy space.

$$\Rightarrow \Omega(E) = \omega(E) dE$$

where $\Omega(E)$ depends on the size of dE , but $\omega(E)$ is independent of the increment size.

- For a system whose energy is constrained to the interval $[E - \Delta E, E]$, the number of microstates with energies in the interval are denoted by $\Omega_{\Delta E}(E)$, and is called the number of accessible states.

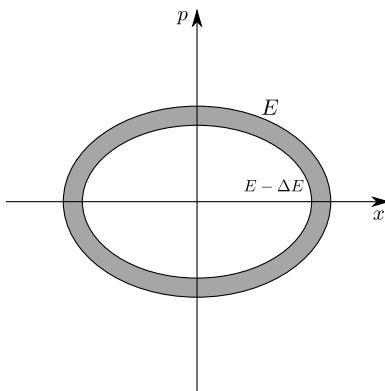
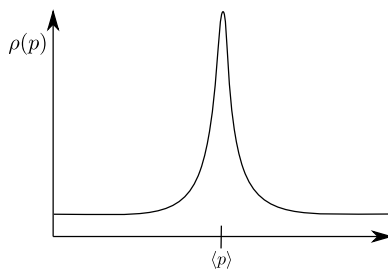


Figure 1.4: Example with Classic Harmonic Oscillator

Remark 1: For macroscopic systems, any reasonable choice of ΔE has $\Omega(E) \approx \Omega_{\Delta E}(E)$ to tremendous accuracy. Thus it is often unnecessary to distinguish between $\Omega(E)$ and $\Omega_{\Delta E}(E)$.

Remark 2: For large systems (N particles, $N \gg 1$), $\Omega(E)$ increases exponentially with N , and for fixed $\frac{E}{N} = \text{const}$, then $\Omega(E)$ and $\omega(E)$ are rapidly growing functions of energy.

Remark 3: The goal of a statistical description is to determine probability distributions for the values of an observable system that is characterized by certain macroscopically defined conditions.



1.3.2 The Equilibrium State

Definition 1: A system is isolated if it can not exchange energy with its surroundings (except for infinitesimal perturbations due to the butterfly effect).

Remark 1: A completely isolated system would, in general, behave very differently from the realistic “isolated” system above.

Definition 2: A system is in equilibrium if the probability of finding the system in a particular microstate does not change with time.

Remark 2: In equilibrium, all probability distributions are time independent, and thus all average values of observables are time independent as well. However, the actual values still can fluctuate (equilibrium is *not* a static state).

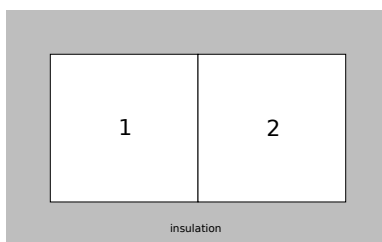
Postulate of Equal a priori Probabilities: An isolated system in equilibrium is equally likely to be found in any of its accessible states.

Postulate - An Approach to Equilibrium: An isolated system that is not in equilibrium will approach equilibrium if left undisturbed for a sufficiently long time.

Remark 3: The above postulate would be false for truly isolated systems.

1.3.3 Interacting Systems

Two systems that are in contact with one another but isolated from the rest of the world can exchange energy in the form of heat (Q) and/or work (W). Thus the energy of each subsystem is not fixed.



Definition 1: The average energy of a system that is a subsystem of a larger isolated system is called its internal energy, and is denoted by $U \equiv \langle E \rangle$.

Remark 1: If a system absorbs heat Q and does work W , then its internal energy changes $\Delta U = Q - W$. (1st law of thermo)

Remark 2: If the change is infinitesimal, then

$$dU = \delta Q - \delta W$$

where dU is an exact differential while δQ and δW are *not*.

Remark 3: ΔU depends only on the systems initial and final states, while Q and W also depend on the process that takes the system from the initial to final state.

1.3.4 Reversible vs Irreversible Processes

Definition 1:

- A quasi-static process is one that is infinitesimally slow enough so that the system remains in equilibrium at all times.
- An adiabatic process does not involve heat transfer.
- A reversible process is both quasi-static and adiabatic.

Remark 1: Let Ω_i and Ω_f be the initial and final number of accessible states in a process. For processes that are adiabatic and quasi-static, $\Omega_i = \Omega_f$, and are thus reversible.

Remark 2: Let x be an external parameter and let $E_n(x)$ be the energy of the n^{th} microstate as a function of x . If x changes quasi-statically, then the sytem does work:

$$\delta W = - \left\langle \frac{\partial E_n}{\partial x} \right\rangle dx := F dx$$

where

$$F := - \left\langle \frac{\partial E_n}{\partial x} \right\rangle$$

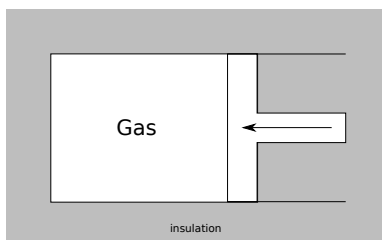
and is called the generalized force conjugate to x .

Example: If the system volume changes by an amount dV , then work is done:

$$\delta W = p dV, \quad \text{with} \quad p = - \left\langle \frac{dE}{dV} \right\rangle$$

where p = pressure is the generalized force conjugate to the volume.

Example: The infinitely slow compression of a gas in a thermally insulated cylinder by a thermally insulated piston is reversible.



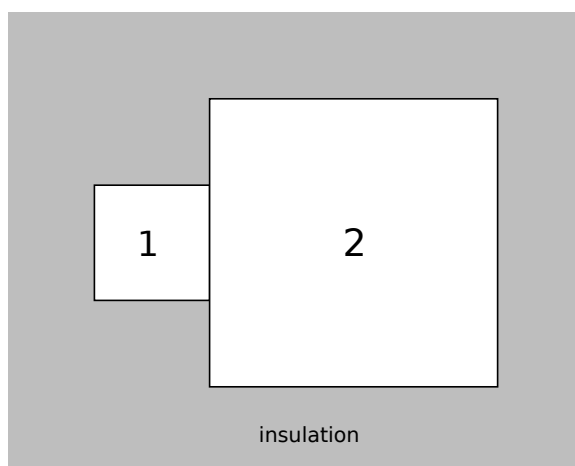
Definition 2: An irreversible process is one that increases the number of accessible states such that $\Omega_f > \Omega_i$.

Remark 3: $\Omega_f > \Omega_i$ implies that the final state has a higher probability and thus the system will not spontaneously return to the initial state.

Example: Humpty Dumpty or the free expansion of a gas into a vacuum are examples of irreversible processes.

1.3.5 Energy, Temperature, and Entropy

Consider a “small” system (1), and a “large” system (2) that are in thermal contact. Let their energies be E_1 and E_2 and the total energy $E_{tot} = E_1 + E_2$ and their number of accessible states are Ω_1 and Ω_2 . Let $E_1 = E$, then the total number of accessible states for



the whole system:

$$\Omega_{tot}(E) = \Omega_1(E)\Omega_2(E_{tot} - E)$$

Remark 1: The total number of states for the whole system is

$$\Omega_{tot} = \sum_E \Omega_{tot}(E)$$

and the probability distribution for E is

$$\rho(E) = \frac{\Omega_{tot}(E)}{\Omega_{tot}}$$

Remark 2: Recall from §1.3.1.R2, we expect $\Omega_{tot}(E)$ to be sharply peaked about $\langle E \rangle = U$, the internal energy of system 1.

Definition 1: A system's entropy is given by:

$$S := k_B \ln(\Omega(E))$$

where $k_B = 1.38 \times 10^{-23} \frac{J}{K}$ = Boltzmann's constant.

Remark 3: For two combined systems, $\Omega = \Omega_1 \Omega_2 \Rightarrow S = S_1 + S_2$, and thus entropy is additive.

Remark 4: The entropy change for any process that takes an isolated system from one macrostate to another is positive semi-definite: $\Delta S \geq 0$, where the equality only holds if the process is reversible.

Definition 2: The temperature, T , of a system is defined as

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{E=U} = k_B \left. \frac{\partial(\ln \Omega)}{\partial E} \right|_{E=U}$$

Also, let

$$\beta := \frac{1}{k_B T}$$

Remark 5: For two systems in equilibrium, the equilibrium state (most probable) occurs when

$$\Omega_1(E) \Omega(E_{tot} - E)$$

is maximized. Which also implies

$$S_1(E) + S_2(E_{tot} - E)$$

is maximized. Taking the derivatives to find the max:

$$\frac{\partial}{\partial E} [S_1(E) + S_2(E_{tot} - E)] = \frac{\partial S_1}{\partial E} - \frac{\partial S_2}{\partial E} = 0$$

$$\Rightarrow T_1 = T_2 \quad \text{in equilibrium}$$

Remark 6: If x is the value of some external parameter, then let $\Omega(E, x)$ be the corresponding number of accessible states. Then the generalized force conjugate to x is given by

$$F = \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial x}$$

Remark 7: The relation between temperature, any external parameter, and the generalized conjugate forces,

$$T = T(x, F)$$

is called the equation of state.

Remark 8: Knowledge of $\Omega(E, x)$ or, equivalently, $S(E, x) = k_B \ln \Omega(E, x)$, is sufficient for calculating all the thermodynamic properties. In particular:

$$\beta = \left. \frac{\partial \ln \Omega}{\partial E} \right|_{E=U}; \quad \frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{E=U}$$

$$F = \left. \frac{1}{\beta} \frac{\partial \ln \Omega}{\partial x} \right|_{x=\langle x \rangle} = T \left. \frac{\partial S}{\partial x} \right|_{x=\langle x \rangle}$$

1.3.6 The Laws of Thermodynamics

First Law:

- For an isolated system, U is a constant.
- If a system is brought from one macrostate to another by a process that causes the system to absorb heat Q and do work W , then the internal energy changes by $\Delta U = Q - W$.

Remark 1: The first law simply expresses energy conservation.

Second Law:

- For any process that can take an isolated system from one macrostate to another, $\Delta S \geq 0$.
- A quasi-static process during which a system absorbs an infinitesimal amount of heat δQ gives an entropy change $dS = \frac{\delta Q}{T}$.

Remark 2: dS is an exact differential, but δQ is not.

Remark 3: The 2nd law has profound technical consequences, which will be covered later in the semester.

Remark 4: Combining the first and second laws gives

$$dU = T dS - \delta W$$

If the work done is purely mechanical, then $\delta W = p dV$

$$\Rightarrow dU = T dS - p dV$$

Third Law: $S(T \rightarrow 0) \rightarrow 0$ (Also called Nerst's Law)

Remark 5: Dropping the distinction between $\Omega(E)$ and $\Omega_{\Delta E}(E)$ is *not* compatible with the 3rd law. More generally, entropy can not be defined in a classical context (more on that later!).

1.3.7 Thermodynamic Potentials

Definition 1: In addition to internal energy, we define:

- Enthalpy: $H = U + pV$
- Helmholtz Free Energy: $F = U - TS$
- Gibb's Free Energy: $G = H - TS$

Remark 1: These are obtained from Legendre transforms of the 1st law. For example:

$$\begin{aligned} dU &= T dS - p dV \\ &= T dS - d(pV) + V dp \\ d(U + pV) &= T dS + V dp \\ &= dH \end{aligned}$$

Similar transforms give F and G . These give the differentials:

$$\begin{aligned} dH &= T dS + V dp \\ dF &= S dT - p dV \\ dG &= -S dT + V dp \end{aligned}$$

Remark 2: These relations imply

$$T = \left(\frac{\partial H}{\partial S} \right)_p = \left(\frac{\partial U}{\partial S} \right)_V$$

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = - \left(\frac{\partial U}{\partial V} \right)_S$$

etc. They also imply Maxwell's Relations:

$$\Rightarrow \left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

$$\left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$$

Remark 3: The specific heats are given by:

$$C_v = \left(\frac{\delta Q}{dT} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$C_p = \left(\frac{\delta Q}{dT} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p$$

1.3.8 The Simple Example: The Ideal Gas

A monatomic ideal gas with N particles has equation of state:

$$PV = nk_B T = nRT$$

It has internal energy

$$U = \frac{3}{2} N k_B T$$

and specific heat / mol:

$$C_V = \frac{3}{2} R$$

$$C_p = \frac{5}{2} R$$

Note that these are only valid for monatomic gas. Now, a quasi-static change from (T_i, V_i) to (T_f, V_f) gives an entropy change of:

$$\Delta S = n C_V \ln \left(\frac{T_f}{T_i} \right) + n R \ln \left(\frac{V_f}{V_i} \right)$$

Remark 1: All of this can be derived from

$$\Omega(E) = V^N \chi(E)$$

where $\chi(E)$ is not an explicit function of V .

1.4 Statistical Ensembles

1.4.1 Gibbsian Ensembles

Consider a system in a particular microstate.

Definition 1: A statistical ensemble consists of many identical systems (same number of particles governed by the same equations of motion) that are all in the same macrostate but, in general, in different microstates.

Remark 1: This concept makes averaging easier since we can average over members of the ensemble at a given time rather than following the time evolution of a single system and averaging over long time periods.

Example: Probability of getting a 6 when rolling 1 die once. You can either roll one die many times, or roll many identical dice at once.

Remark 2: Need to find the probability of a member of the ensemble to be in a certain microstate. This depends on the physical situation.

1.4.2 The Microcanonical Ensemble

Consider an isolated system in equilibrium whose microstates have energies

$$E(p, q) \quad \text{for the classical case, or}$$

$$E_n, \quad n = 0, 1, \dots \quad \text{for the quantum mechanical case}$$

Define a macrostate by demanding that the energy lies in an interval $[E - \Delta E, E]$.

Theorem: The probability of the system being in the microstate with energy $E(p, q)$ or E_n is:

$$\rho(p, q) = \frac{1}{\int d\gamma} \cdot \begin{cases} 1 & \text{if } E - \Delta E \leq E(p, q) \leq E \\ 0 & \text{otherwise} \end{cases} \quad (\star)$$

where the integral is taken over the region where $E - \Delta E \leq E(p, q) \leq E$ and

$$\gamma \equiv (p, q), \quad d\gamma = dpdq, \quad \Gamma = \{\gamma\}$$

$$\rho(E_n) = \frac{1}{\sum 1} \cdot \begin{cases} 1 & \text{if } E - \Delta E \leq E_n \leq E \\ 0 & \text{otherwise} \end{cases} \quad (\star)$$

Proof: Follows from §1.3.2.P1.

Remark 1:

$$\int \rho(p, q) d\gamma = 1; \quad \sum_n \rho(E_n) = 1$$

And so our normalization is ok.

Remark 2: This ensemble is called microcanonical and (\star) is called the microcanonical distribution function. It is appropriate for isolated systems.

Remark 3: Microcanonical ensembles lack an obvious temperature concept.

1.4.3 The Canonical Ensemble

Definition 1: A heat bath is a system that is large enough so that any heat that is absorbed or given off by the heat bath in any thermodynamic process is negligible compared to its internal energy.

Definition 2: The canonical partition function, Z , is defined quantum mechanically as:

$$Z = \sum_n e^{-\beta E_n}$$

and classically, for a system with N particles and $3N$ degrees of freedom, as:

$$Z = \frac{1}{h^{2N} N!} \int e^{-\beta E(\gamma)} d\gamma$$

Remark 1: The uncertainty relation implies that the phase space can not be partitioned into cells smaller than $\Delta p \Delta q = \hbar$. Thus the factor of \hbar^{2N} in the classical definition. We'll discuss the origin of the $N!$ later.

Remark 2: A more general definition of the partition function which holds classically and quantum mechanically is:

$$Z = \int_0^\infty \omega(E) e^{-\beta E} dE$$

where $\omega(E)$ is the density of states.

Theorem: For a system that is in thermal contact with a heat bath, the probability of being in a microstate with energy E_n (QM) is:

$$\rho_n = \frac{1}{Z} e^{-\beta E_n} \quad (\star\star)$$

or classically:

$$\rho_E = \frac{1}{h^{3N} N! Z} e^{-\beta E} \quad (\star\star)$$

where $\beta = \frac{1}{k_B T}$ and T is the temperature of the heat bath.

Proof (QM only): Let 1 = system and let 2 = heat bath. Thus we have that 1 is in a state with energy E_n , and 2 has energy E_2 . Thus, the combined system has

$$\begin{aligned} E_{tot} &= E_n + E_2 \\ &= \text{constant by 1st law} \end{aligned}$$

By §1.3.2.P1, we have that

$$\begin{aligned} \rho_n &= (\text{const}) \Omega_2(E_{tot} - E_n) \\ \Rightarrow \rho_n &= (\text{const}) \exp \left[\frac{S_2(E_{tot} - E_n)}{k_B} \right] \end{aligned}$$

Because of the heat bath, $E_{tot} \gg E_n$, so:

$$\begin{aligned} \rho_n &= (\text{const}') \exp \left[-E_n \underbrace{\frac{\partial S_2}{\partial E_n} \bigg|_{E_{tot}}}_{\beta} \frac{1}{k_B} + \dots \right] \\ &= (\text{const}') e^{-\beta E_n} \end{aligned}$$

Normalization implies

$$(\text{const}') = \left(\sum_n e^{-\beta E_n} \right)^{-1} = \frac{1}{Z}$$

Remark 3: This is called a canonical ensemble and $(\star\star)$ is a canonical distribution or a Gibbs-Boltzmann distribution.

Remark 4: The canonical distribution also applies to situations where the system has been prepared so that its energy is not known precisely but the average energy, U , is known. In this case, T is the temperature a heat bath needs to have in order for the average energy to remain U if the system is brought into contact with the heat bath.

Remark 5: The energy of a system in contact with a heat bath is *not* fixed, but is subject to fluctuations. How big are these fluctuations?

Lemma: In a canonical ensemble, the mean energy and the rms energy fluctuations are determined by the partition function via the following relationships:

$$U = \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

$$(\Delta E) = \left\langle (E - \langle E \rangle)^2 \right\rangle^{1/2} = \left(\frac{\partial^2 \ln Z}{\partial \beta^2} \right)^{1/2}$$

Proof:

$$Z = \sum_n e^{-\beta E_n}$$

Thus

$$\begin{aligned} -\frac{\partial \ln Z}{\partial \beta} &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \\ &= \frac{1}{Z} \sum_n E_n e^{-\beta E_n} \\ &= \sum_n E_n \rho_n \\ &= \langle E \rangle \end{aligned}$$

And

$$\begin{aligned} \frac{\partial^2 \ln Z}{\partial \beta^2} &= \frac{\partial}{\partial \beta} \left[-\frac{1}{Z} \sum_n E_n e^{-\beta E_n} \right] \\ &= \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right) \sum_n E_n e^{-\beta E_n} + \frac{1}{Z} \sum_n E_n^2 e^{-\beta E_n} \\ &= -\langle E \rangle \frac{1}{Z} \sum_n E_n e^{-\beta E_n} + \langle E^2 \rangle \\ &= -\langle E \rangle^2 + \langle E^2 \rangle \\ &= (\Delta E) \end{aligned}$$

Remark 6: The heat capacity, $C_V = \left(\frac{dU}{dT} \right)_V$:

$$\Rightarrow C_V = -\frac{\beta}{T} \left(\frac{\partial U}{\partial \beta} \right)_V = \frac{\beta}{T} (\Delta E)^2$$

Remark 7: For a macroscopic system with N particles at temperature T ,

$$U = \mathcal{O}(Nk_B T)$$

$$C_V = \mathcal{O}(Nk_B)$$

Proposition 1: The energy fluctuations in a large system described by a canonical ensemble are gaussian, and the relative energy fluctuations are:

$$\frac{\Delta E}{\langle E \rangle} = \mathcal{O} \left(\frac{1}{\sqrt{N}} \right)$$

with N equalling the number of particles. So the fluctuations are small, and thus we need only worry about the averages.

Proof: Consider a large system, and divide it up into n identical subsystems that are each still macroscopic (and $n \gg 1$). Let each subsystem have energy E_i , ($i =$

1	2	3	...	
			...	n

$1, \dots, n$). Thus, the total energy of the system is:

$$E_{tot} = \sum_{i=1}^n E_i$$

Due to fluctuations, E_i are random variables that obey the canonical distribution. Thus each subsystem has a canonical partition function:

$$z_i = \sum_m e^{-\beta E_m^{(i)}}$$

where $E_m^{(i)}$ is the energy of subsystem number i . The subsystems are identical, and thus $z_i = z$. Thus, the partition function of the whole system can be written:

$$Z = z^n$$

The canonical distribution has a finite variance, and hence CLT applies. By §1.2.6, we have:

$$x_i = nE_i \quad (i = 1, \dots, n)$$

$$y = \frac{1}{n} \sum_{i=1}^n x_i = E$$

$$\Rightarrow \rho(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp \left[\frac{-(E - \langle E \rangle)^2}{2\sigma^2} \right]$$

with

$$\sigma^2 = \sum_{i=1}^n \left(\langle E_i^2 \rangle - \langle E_i \rangle^2 \right) = n \langle (E - \langle E \rangle)^2 \rangle = n(\Delta E)^2$$

By the above Lemma:

$$\sigma^2 = \frac{n\partial^2 \ln z}{\partial \beta^2} = \frac{\partial^2 \ln Z}{\partial \beta^2} = (\Delta E_{tot})^2 = \frac{T}{\beta} C_V$$

$$\Rightarrow \frac{(\Delta E_{tot})^2}{\langle E \rangle^2} = \frac{\sigma^2}{U^2} = \frac{1}{U^2} \frac{T}{\beta} C_V = \mathcal{O} \left[\frac{T}{N k_B T} \frac{k_B T}{N k_B T} N k_B \right] = \mathcal{O} \left[\frac{1}{N} \right]$$

Remark 8: A macroscopic system has an extremely sharp gaussian energy distribution.

Proposition 2: In a canonical ensemble, the Helmholtz free energy is given by:

$$F = -k_B T \ln Z$$

Proof: Let x be an external parameter that characterizes the system. Then the energy level $E_n = E_n(x)$.

$$\Rightarrow Z = \sum_n e^{-\beta E_n(x)} = Z(\beta, x)$$

If we change x, β quasi-statically by dx and $d\beta$ respectively, then

$$\begin{aligned} d \ln Z &= \frac{\partial \ln Z}{\partial \beta} d\beta + \frac{\partial \ln Z}{\partial x} dx \\ &= -U d\beta + \frac{1}{Z} \sum (-\beta) e^{-\beta E_n(x)} \frac{\partial E}{\partial x} dx \\ &= -U d\beta - \beta \left\langle \frac{\partial E_n}{\partial x} \right\rangle dx \end{aligned}$$

By §1.3.4.R2:

$$\begin{aligned} &= -U d\beta + \beta \delta W \\ &= \beta \delta W - d(U\beta) + \beta dU \\ &= \beta (\delta W + dU) - d(U\beta) \\ &= \beta (\delta Q) - d(U\beta) \\ &= \frac{1}{k_B T} T dS - d(U\beta) \\ \Rightarrow d(\ln Z + U\beta) &= \frac{1}{k_B} dS \\ \Rightarrow S &= k_B (\ln Z + \beta U) = k_B \ln Z + \frac{U}{T} \quad (\text{up to a constant}) \end{aligned}$$

Thus by the definition of F :

$$\begin{aligned} F &= U - TS \\ &= -k_B T \ln Z \end{aligned}$$

Remark 9: F , and therefore Z , determine all thermodynamic quantities.

Corollary 1: Up to a constant,

$$S = k_B \ln Z + k_B T \frac{\partial \ln Z}{\partial T}$$

Proof: By §1.3.7:

$$S = -\frac{\partial F}{\partial T} = k_B \ln Z + k_B T \frac{\partial \ln Z}{\partial T}$$

Corollary 2::

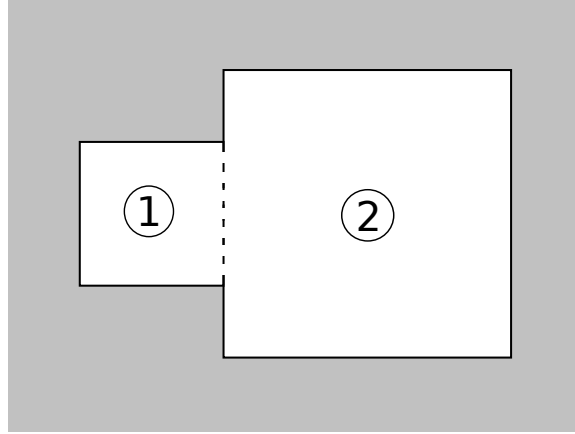
$$p = k_B T \frac{\partial \ln Z}{\partial V}$$

Proof: Also by §1.3.7:

$$p = -\frac{\partial F}{\partial V} = \frac{\partial}{\partial V} (k_B T \ln Z) = k_B T \frac{\partial \ln Z}{\partial V}$$

1.4.4 The Grand Canonical Ensemble

Consider System ① in contact with a heat bath (System ②):



In this case, due to the perforated boundry, both heat and particles can be exchanged.

Remark 1: The particle number N is not fixed, and so the number of accessible states depends on both N and E .

$$\Rightarrow \Omega = \Omega(E, N)$$

Definition 1: The chemical potential, μ , of a system is

$$\mu := -\frac{1}{\beta} \frac{\partial \ln \Omega}{\partial N} \bigg|_{\substack{E=\langle E \rangle=U \\ N=\langle N \rangle}}$$

Remark 2: $-\beta\mu$ is related to N as β is related to energy (§1.3.5.R8):

$$\beta = \left. \frac{\partial \ln \Omega}{\partial E} \right|_{E=U}, \quad -\beta\mu = \left. \frac{\partial \ln \Omega}{\partial N} \right|_{\substack{E=U \\ N=\langle N \rangle}}$$

Remark 3: Many properties of β carry over to μ . In particular, two systems in equilibrium with one another have the same μ . In addition, a heat bath will have constant μ .

Definition 2: Let $E_n^{(N)}$ ($n = 0, 1, \dots$) be the energy levels of ① when it contains N particles. The grand canonical partition function is defined as

$$Z = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{n=0}^{\infty} e^{-\beta E_n^{(N)}}$$

Remark 4: Here we restrict ourselves to quantum mechanics.

Theorem: The probability of system ① being in a macrostate with N particles and energy $E_n^{(N)}$ is

$$\rho_n^{(N)} = \frac{1}{Z} \exp \left[-\beta \left(E_n^{(N)} - \mu N \right) \right]$$

Proof: Generalizing §1.4.3, we have that

$$E_n^{(N)} + E_2 = E_{tot}$$

$$N + N_2 = N_{tot}$$

$$\begin{aligned} S_2(E_2, N_2) &= k_B \ln \Omega_2 \left(E_{tot} - E_n^{(N)}, N_{tot} - N \right) \\ &\approx k_B \ln \Omega_2(E_{tot}, N_{tot}) - k_B E_n^{(N)} \left. \frac{\partial \ln \Omega_2}{\partial E} \right|_{\substack{E_{tot} \\ N_{tot}}} - k_B N \left. \frac{\partial \ln \Omega_2}{\partial N} \right|_{\substack{E_{tot} \\ N_{tot}}} \\ &= \mathcal{C} - k_B \beta E_n^{(N)} + k_B N \beta \mu \end{aligned}$$

$$\Rightarrow \rho_n^{(N)} \sim \Omega_2 = e^{S_2/k_B} = \mathcal{C}' e^{-\beta E_n^{(N)}} e^{\beta \mu N}$$

where \mathcal{C} is a constant. Normalizing, we find that

$$\mathcal{C}' = \frac{1}{Z}$$

Lemma: In a grand canonical ensemble, the thermodynamic potentials U, H, F, G obey the relations:

$$\begin{aligned} dU &= T dS - p dV + \mu dN, & U(S, V, N) \\ dH &= T dS + V dp + \mu dN, & H(S, p, N) \\ dF &= -S dT - p dV + \mu dN, & F(T, V, N) \\ dG &= -S dT + V dp + \mu dN, & G(T, p, N) \end{aligned}$$

Proof: Recall that

$$\begin{aligned} \mu &= -k_B T \left. \frac{\partial \ln \Omega}{\partial N} \right|_{\substack{E=U \\ N=\langle N \rangle}} \\ \mu &= -T \left(\frac{\partial S}{\partial N} \right)_{U,V} \end{aligned}$$

But then

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial E} \right)_{V,N} \Big|_{E=U} dU + \left(\frac{\partial S}{\partial V} \right)_{U,N} dV + \left(\frac{\partial S}{\partial N} \right)_{U,V} dN \\ &= \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN \\ &\Rightarrow dU = T dS - p dV + \mu dN \end{aligned}$$

Performing Legendre transformations, it follows that:

$$\begin{aligned} H &= U + PV \Rightarrow dH = T dS + V dp + \mu dN \\ F &= U - TS \Rightarrow dF = -S dT - p dV + \mu dN \\ G &= F + pV \Rightarrow dG = -S dT + V dp + \mu dN \end{aligned}$$

Remark 5: μ is the energy change that results from adding one particle to the system adiabatically ($dS = 0$) and isochorically ($dV = 0$).

Lemma 2: The Duham-Gibbs Relation:

$$G = N\mu$$

Proof: By Lemma 1:

$$G = G(T, p, N)$$

We expect G to be proportional to N , and so we let

$$G(T, p, N) = N g(T, p) \quad (\star)$$

Now, again by Lemma 1:

$$\begin{aligned}\mu &= \left(\frac{\partial G}{\partial N} \right)_{T,p} = g(T, p) = \frac{G}{N} \\ &\Rightarrow G = \mu N\end{aligned}$$

Remark 6: It is not obvious that (\star) holds. See §1.4.5 for a discussion and derivation of (\star) .

Proposition 1: In a grand canonical ensemble:

$$J := -k_B T \ln Z$$

defines a thermodynamic potential whose differential is

$$dJ = -S dT - p dV - N d\mu$$

which is also equal to

$$J = -pV$$

This is called the grand potential.

Proof: Perform a Legendre transformation from $F = F(T, V, N)$ to $J = F - \mu N = J(T, V, \mu)$.

$$\begin{aligned}\Rightarrow dJ &= dF - \mu dN - N d\mu \\ &= -S dT - p dV - N d\mu\end{aligned}$$

From Lemma 2 ($G = \mu N$):

$$\Rightarrow J = F - \mu N = F - G = F - (F + pV) = -pV$$

We must still show that:

$$J = -k_B T \ln Z$$

Now

$$\begin{aligned}\rho_n^{(N)} &= \frac{1}{Z} \exp \left[-\beta E_n^{(N)} + \beta \mu N \right] \\ &\sim \Omega_2 \left(E_{tot} - E_n^{(N)}, N_{tot} - N \right) \\ &\sim \frac{\Omega_{tot}}{\Omega_1(E_n^{(N)}, N)} \\ \Rightarrow \ln \rho_n^{(N)} &= \mathcal{C} + \ln \Omega_{tot} - \ln \Omega_1 \left(E_n^{(N)}, N \right)\end{aligned}$$

$$\begin{aligned}
\Rightarrow S &= k_B \left\langle \ln \Omega_1 \left(E_n^{(N)}, N \right) \right\rangle = - \left\langle \ln \rho_n^{(N)} \right\rangle \quad \text{up to a const} \\
&= k_B \ln Z + k_B \beta \left\langle E_n^{(N)} \right\rangle - k_B \beta \mu \langle N \rangle
\end{aligned}$$

Multiplying everything by $(-T)$ yields

$$\begin{aligned}
-k_B T \ln Z &= TS + U - \mu \langle N \rangle \\
&= F - \mu \langle N \rangle \\
&= J
\end{aligned}$$

Proposition 2: In a grand canonical ensemble, the mean particle number is given by

$$\begin{aligned}
\langle N \rangle &= k_B T \frac{\partial \ln Z}{\partial \mu} \\
Z &= \sum_N e^{\beta \mu N} \sum_n e^{-\beta E_n^{(N)}}
\end{aligned}$$

Proof: See HW.

1.4.5 The Thermodynamic Limit and the Durham-Gibbs Relation

Consider a macroscopic system, $V = \mathcal{O}(1 \text{ cm}^3)$, $N = \mathcal{O}(10^{20})$, which is huge compared to its microscopic dimensions of $N \sim \mathcal{O}(1)$, $V \sim \mathcal{O}(1 \text{ \AA}^3)$. Recall that the free energy is $F = F(T, V, N)$.

Definition 1: The limit as $V \rightarrow \infty$ and $N \rightarrow \infty$ so that $n = \frac{N}{V} = \mathcal{C}$ and $f = \frac{F}{V} = \mathcal{C} < \infty$ is called the thermodynamic limit.

Remark 1: For practical purposes, macroscopic systems are in the thermodynamic limit.

Definition 2:

- Consider a function of n variables, $f(x_1, \dots, x_n)$. It is a homogeneous function of degree a if the number $a \in \mathbb{R}$ exists so that

$$f(bx_1, \dots, bx_n) = b^a f(x_1, \dots, x_n) \quad \forall b > 0$$

- f is a generalized homogeneous function if $n+1$ numbers $[x_1], [x_2], \dots, [x_n], [f]$ (not all zero) exist so that for all $b > 0$

$$f(b^{[x_1]}x_1, b^{[x_2]}x_2, \dots, b^{[x_n]}x_n) = b^{[f]}f(x_1, x_2, \dots, x_n)$$

Examples:

1. If we have the case where $n = 1$, $f(x) = cx^a$

$$\Rightarrow f(bx) = c(bx)^a = b^a cx^a = b^a f(x)$$

\Rightarrow homogeneous function of degree a

If instead we had $n = 1$, $f(x) = \ln(x)$:

$$\Rightarrow f(bx) = \ln(bx) = \ln b + \ln x$$

\Rightarrow Not homogeneous

2. Now consider when $n = 2$, $f(x, y) = x^3 + xy + y^{3/2}$. Let's choose $[x] = 1$, $[y] = 2$.

$$\begin{aligned} \Rightarrow f(b^{[x]}x, b^{[y]}y) &= f(bx, b^2y) \\ &= (bx)^3 + (bx)(b^2y) + (b^2y)^{3/2} \\ &= b^3 \left(x^3 + xy + y^{3/2} \right) \\ &= b^3 f(x, y) \end{aligned}$$

$\Rightarrow f(x, y)$ is a generalized homogeneous function with $[f] = 3$.

What if we hadn't known what $[x]$ and $[y]$ were?

$$x^3 b^{3[x]} + b^{[x]+[y]}xy + b^{3[y]/2}y^{3/2} = b^{[f]}(x^3 + xy + y^{3/2})$$

$$\Rightarrow [x] + [y] = 3[x] = \frac{3}{2}[y] = [f]$$

So we basically have 3 equations, 3 unknowns. The solution will be unique up to a redefinition of b . As a counter example, consider:

$$n = 2 : \quad f(x, y) = x^3 + e^y \text{ is not a generalized homogeneous function}$$

Consider now a d -dimensional system in the thermodynamic limit, and change all linear dimensions by a factor of $b > 0$.

$$L \rightarrow L' = \frac{L}{b}$$

$$V \rightarrow V' = b^{-d}V$$

Remark 2: Under this transformation, in order for $n = \frac{N}{V}$ to remain constant, we must have

$$N \rightarrow N' = b^{-d}N$$

Remark 3: If the system is in contact with a heat bath, where the system is huge in comparison to the microscopic limit, and the heat bath is huge in comparison to the system, then T does not change upon changing volume.

$$T \rightarrow T' = b^0 T$$

Lemma: The Helmholtz free energy is a generalized homogeneous function of T, V, N , namely:

$$F(T, V, N) = b^d F(T, Vb^{-d}, Nb^{-d})$$

Proof: By Definition 1:

$$\begin{aligned} \frac{F(T', V', N')}{V'} &= f(T', V', N') \\ &= f(T, V, N) \quad \text{in the thermodynamic limit} \\ &= \frac{F(T, V, N)}{V} \end{aligned}$$

$$\begin{aligned} \Rightarrow F(T, V, N) &= \frac{V}{V'} F(T', V', N') \\ &= b^d F(T, b^{-d}V, b^{-d}N) \end{aligned}$$

Remark 4: $[f] = -d$, $[V] = -d$, $[N] = -d$, $[T] = 0$ are called scale dimensions of F, V, N, T respectively.

Remark 5: Let A and B have scale dimensions of $[A]$ and $[B]$. Then $[AB] = [A] + [B]$.

Lemma 2: There exists a function $\tilde{F}(x, y)$ such that

$$F(T, V, N) = N \tilde{F}\left(T, \frac{V}{N}\right)$$

Proof: The value of b in Lemma 1 is arbitrary so long as it remains positive. Thus, let's let $b = N^{1/d}$.

$$\Rightarrow F(T, V, N) = NF(T, N^{-1}V, 1)$$

Define $F(x, y, 1) := \tilde{F}(x, y)$.

$$\Rightarrow F(T, V, N) = N \tilde{F}\left(T, \frac{V}{N}\right)$$

Lemma 3:

$$N \left(\frac{\partial F}{\partial N} \right)_{V,T} + V \left(\frac{\partial F}{\partial V} \right)_{N,T} = F$$

Proof: By Lemma 2:

$$\begin{aligned} \left(\frac{\partial F}{\partial N} \right)_{V,T} &= \tilde{F} \left(T, \frac{V}{N} \right) + N \left(\frac{-V}{N^2} \right) \frac{\partial \tilde{F}(x, y)}{\partial y} \bigg|_{\substack{x=T \\ y=V/N}} \\ &= \tilde{F} \left(T, \frac{V}{N} \right) - \frac{V}{N} \left(\frac{\partial \tilde{F}(x = T, y = V/N)}{\partial y} \right) \end{aligned}$$

Since

$$\begin{aligned} \left(\frac{\partial F}{\partial N} \right)_{V,T} &= N \frac{1}{N} \frac{\partial \tilde{F}}{\partial y} \\ \Rightarrow N \left(\frac{\partial F}{\partial N} \right)_{V,T} + V \left(\frac{\partial F}{\partial V} \right)_{N,T} &= N \tilde{F} \left(T, \frac{V}{N} \right) = F(T, V, N) \end{aligned}$$

Theorem: Again, $G = \mu N$ by the Duham-Gibbs Relation.

Proof: By §4.4.L1 $\Rightarrow dF = -S dT - p dV + \mu dN$.

$$\Rightarrow p = - \left(\frac{\partial F}{\partial V} \right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}$$

Now

$$\begin{aligned} G &= F + pV \\ &= F - \left(\frac{\partial F}{\partial V} \right)_{T,N} V \\ &= N \left(\frac{\partial F}{\partial N} \right)_{T,V} + V \left(\frac{\partial F}{\partial V} \right)_{T,N} - V \left(\frac{\partial F}{\partial V} \right)_{T,N} \quad \text{by above L3} \\ &= N \left(\frac{\partial F}{\partial N} \right)_{T,V} \\ &= \mu N \end{aligned}$$

Remark 6: The above proof did *not* use §4.4(★). ($G(T, p, N) = Ng(T, p)$)

Remark 7: §4.4(★) can be obtained as follows:

$$[F] = [V] = -d$$

$$\Rightarrow [p] = \left[\frac{\partial F}{\partial V} \right] = \left[\frac{F}{V} \right] = [F] - [V] = 0$$

$$\begin{aligned} \Rightarrow G(T, p, N) &= -b^{-[G]} G(Tb^{[T]}, pb^{[p]}, Nb^{[N]}) \\ &= b^d G(T, p, Nb^{-d}) \end{aligned}$$

Let $b = N^{1/d}$:

$$\Rightarrow G(T, p, N) = NG(T, p, 1) := Ng(T, p)$$

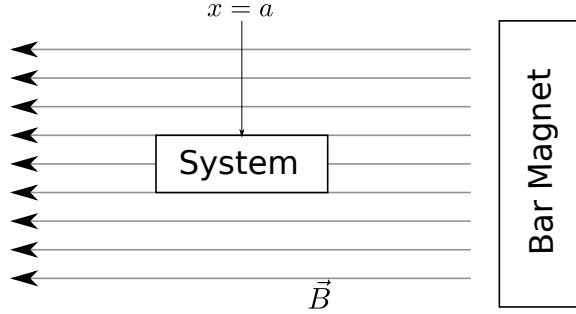
where $g(x, y) := G(x, y, 1)$. Thus the proof of the Duham-Gibbs relation in §4.4 was indeed true, just not obvious.

1.4.6 Systems in Magnetic Fields

In general, work is not purely mechanical for systems in magnetic fields.

Lemma: A magnetization change $d\mathbf{M}$ by a magnetic field requires work $\delta W = \mathbf{B} \cdot d\mathbf{M}$.

Proof: We want to magnetize the system by letting it approach the bar magnet from $x = -\infty$. Let the field be axi-symmetric along the x-axis and $B(x \rightarrow \infty) \rightarrow 0$.



Also let the final position by $x = a$. The attractive force at point x is:

$$F = M(x) \frac{dB}{dx}$$

To do this process quasi-statically, we need a balancing force $F_{balance} = -F$. So we want to apply force:

$$F_{balance}(x) = -M(x) \frac{dB}{dx}$$

which does work

$$\begin{aligned}
 W_1 &= - \int_{-\infty}^a M(x) \frac{dB}{dx} dx \\
 &= -M(a)B(a) + \int_{-\infty}^a \frac{dM}{dx} B(x) dx \quad (\text{int by parts}) \\
 &= -M(a)B(a) + \int_0^{M(a)} B(x) dM
 \end{aligned}$$

To find the work it takes to magnetize the system in the absence of any other changes, we now take the system back to $x = -\infty$ while keeping magnetization fixed at a value $M(a)$. This requires work.

$$\begin{aligned}
 W_2 &= - \int_a^{-\infty} M(a) \frac{dB}{dx} dx \\
 &= -M(a) [0 - B(a)] \\
 &= M(a)B(a)
 \end{aligned}$$

So the total required work to magnetize the system is:

$$W = W_1 + W_2 = \int_0^{M(a)} B(M) dM$$

For an infinitesimal magnetization then, the amount of work done on the system is

$$\delta W = \mathbf{B} \cdot d\mathbf{M}$$

Proposition: For a magnetizable system in a magnetic field, the free energy obeys

$$dF = -S dT - p dV - \mathbf{B} \cdot d\mathbf{M} + \mu dN$$

Proof: $dU = \delta Q - \delta W = T dS - \mathbf{B} \cdot d\mathbf{M}$ for purely magnetic work. The rest follows as before.

Remark 1: By means of a Legendre transformation, $\tilde{F} = F + \mathbf{B} \cdot \mathbf{M}$, one can switch from $F = F(T, V, M, N)$ to $\tilde{F} = \tilde{F}(T, V, B, N)$. Similar things can be done for the other thermodynamic potentials.

1.5 Quantum Statistical Mechanics

1.5.1 The Postulates of Quantum Statistical Mechanics

Let a system at time t be in a quantum state $|\psi(t)\rangle$. Expand this state in a complete set of orthonormal functions $\{|\varphi_n\rangle\}$.

$$|\psi(t)\rangle = \sum_n C_n(t) |\varphi_n\rangle, \quad C_n(t) \in \mathbb{C}$$

Remark 1: $|C_n(t)|^2$ is the probability for a system to be in state $|\varphi_n\rangle$ at time t .

Remark 2: The time evolution of $|\psi(t)\rangle$ is determined by Schrodinger's equation:

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$$

with \hat{H} representing the systems Hamiltonian operator, and we assume \hat{H} to be time-independent. A deterministic system would imply that if you know state $|\psi(0)\rangle$, then you know the system's state at all future times.

Remark 3:

$$\begin{aligned} \langle \varphi_m | \psi(t) \rangle &= \sum_n C_n \langle \varphi_m | \varphi_n \rangle = C_m(t) \\ \Rightarrow i\hbar \dot{C}_n(t) &= \left\langle \varphi_n \left| i\hbar \frac{\partial}{\partial t} \psi(t) \right. \right\rangle = \left\langle \varphi_n \left| \hat{H} \right| \psi(t) \right\rangle \\ &= \sum_m C_m(t) \left\langle \varphi_n \left| \hat{H} \right| \varphi_m \right\rangle \\ &:= \sum_m H_{nm} C_m(t) \end{aligned}$$

where H_{nm} are the matrix elements of the Hamiltonian.

$$\begin{aligned} \Rightarrow \dot{C}_n(t) &= \frac{i}{\hbar} \sum_m H_{nm} C_m(t) \\ \dot{C}_n^* &= \frac{i}{\hbar} \sum_m H_{nm}^* C_m^*(t) \\ &= \frac{i}{\hbar} \sum_m H_{mn} C_m^*(t) \end{aligned}$$

Here $\langle \varphi | \psi \rangle$ is a scalar product in Hilbert space and we have used the fact that \hat{H} is hermitian.

$$\hat{H}^\dagger = \hat{H} \quad \Rightarrow \quad H_{nm}^* = H_{mn}$$

Let \hat{A} be an operator in Hilbert space that corresponds to some observable \mathcal{A} . From Phys 515/516, we know that the expectation of \hat{A} in a state $\psi(t)$ is given by:

$$\begin{aligned} \langle \hat{A} \rangle &= \langle \psi(t) | \hat{A} | \psi(t) \rangle \\ &= \sum_{nm} C_n^*(t) C_m(t) \langle \varphi_n | \hat{A} | \varphi_m \rangle \\ &= \sum_{nm} C_n^*(t) C_m(t) A_{nm} \end{aligned}$$

Remark 4: The normalization of $|\psi(t)\rangle$ implies that

$$\sum_n |C_n(t)|^2 = 1$$

Remark 5: $\langle \hat{A} \rangle$ is the average value obtained for the observable, taken from a large number of simultaneous measurements on equally prepared systems.

Remark 6: Quantum Mechanics implies an averaging concept even in the absence of statistical mechanics considerations.

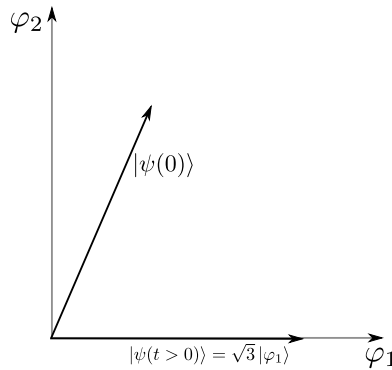
Remark 7: Due to the butterfly effect, we are never quite sure which state the system is in, and therefore we need an ensemble average. Thus the ensemble averaged values of $\langle \hat{A} \rangle$ (which is now a random variable due to butterflies) is:

$$\langle A \rangle = \sum_{nm} \langle C_n^*(t) C_m(t) \rangle A_{nm}$$

For a deterministic quantum mechanical system, $|\psi(t)\rangle$ describes a system for all time given $|\psi(0)\rangle$. For example, let $|\psi(0)\rangle = |\varphi_1\rangle + 2|\varphi_2\rangle$:

$$\begin{aligned} \Rightarrow C_1(t=0) &= 1 \\ C_2(t=0) &= 2 \end{aligned}$$

In 2 dimensional Hilbert space:



The butterfly effect means we are not *exactly* sure what the state of $|\psi(0)\rangle$ is.

$$\Rightarrow \hat{H}_{total} = \hat{H}_{system} + \hat{H}_{system+butflies}$$

Definition 1: The density matrix or statistical operator of the system is defined as the operator $\hat{\rho}$ whose matrix elements are

$$\rho_{nm}(t) = \langle \varphi_n | \hat{\rho} | \varphi_m \rangle := \langle C_m(t) C_n^*(t) \rangle$$

Remark 8: As in §4.1, the average above can be considered either as a time average for one system, or as an ensemble average at a given time.

Proposition 1: Let $\hat{\rho}$ be the statistical operator of some system. Let \hat{A} be an operator that corresponds to observable \mathcal{A} . Then the ensemble average $\langle \hat{A} \rangle$ of the expectation value A of \hat{A} is given by:

$$\langle A \rangle = \text{tr} (\hat{\rho} \hat{A})$$

Proof:

$$\begin{aligned} \text{tr} (\hat{\rho} \hat{A}) &= \sum_n \langle \varphi_n | \hat{\rho} \hat{A} | \varphi_n \rangle \\ &= \sum_n \sum_m \langle \varphi_n | \hat{\rho} | \varphi_m \rangle \langle \varphi_m | \hat{A} | \varphi_n \rangle \\ &= \sum_{nm} \rho_{nm} A_{mn} \\ &= \sum_{nm} \langle C_m(t) C_n^*(t) \rangle A_{mn} \\ &= \sum_{nm} \langle C_n(t) C_m^*(t) \rangle A_{nm} \\ &= \langle A \rangle \end{aligned}$$

Proposition 2: The statistical operator obeys the Liouville - von Neumann equation:

$$i\hbar \partial_t \hat{\rho}(t) = [\hat{H}, \hat{\rho}(t)]$$

Proof:

$$\begin{aligned} i\hbar \partial_t \rho_{nm} &= i\hbar \left(\left\langle \dot{C}_n(t) C_m^*(t) + C_n(t) \dot{C}_m^*(t) \right\rangle \right) \\ &= \sum_s (H_{ns} \langle C_s(t) C_m^*(t) \rangle - H_{sm} \langle C_n(t) C_m^*(t) \rangle) \\ &= \sum_s (H_{ns} \rho_{sm} - \rho_{ns} H_{sm}) \\ &= (\hat{H} \hat{\rho})_{nm} - (\hat{\rho} \hat{H})_{nm} \\ &= [\hat{H}, \hat{\rho}]_{nm} \end{aligned}$$

Corollary 1: For a system in equilibrium, the density matrix commutes with the Hamiltonian, $[\hat{H}, \hat{\rho}] = 0$.

Proof: In equilibrium, $\hat{\rho}$ is *not* a function of time.

$$\Rightarrow \partial_t \hat{\rho}_{eq} = 0 \quad \Rightarrow \quad [\hat{H}, \hat{\rho}] = 0$$

Corollary 2: In equilibrium, $\hat{\rho}$, can depend only on the Hamiltonian and operators that commute with the Hamiltonian. (I.e. that correspond to conserved quantities.)

Let φ_n be energy eigenstates:

$$\hat{H}\varphi_n = E_n\varphi_n$$

Quantum mechanics tell us that, if \hat{A} commutes with \hat{H} , then φ_n can be chosen so that they are eigenstates of both \hat{A} and \hat{H} .

Corollary 3: In this basis, the density operator is diagonal:

$$\rho_{nm} = \delta_{nm}\rho_n$$

where ρ_n is a function of the E_n and of the eigenvalues of any other conserved quantities that $\hat{\rho}$ depends on.

Corollary 4:

$$\text{Liouville's Equation:} \quad \frac{d}{dt}\rho(p, q, t) = 0$$

Postulate 1 - Postulate of Equal a priori Probabilities: For an isolated system in equilibrium:

$$\rho_n = \rho(E_n)$$

with ρ_n given by equation (★) in §4.2.

Remark 9: “Isolated” means isolated up to the butterfly effect.

Postulate 2 - Approach to Equilibrium: This is the exact same as done in §1.3.2.P2.

Remark 10: Remaining job: to find the statistical operator for systems that are *not* isolated.

1.5.2 The Density Matrix for Various Ensembles

Microcanonical Ensemble: By §5.1, the statistical operator in terms of its matrix elements in a basis of energy eigenstates is:

$$\rho_n = \frac{1}{\sum 1} \begin{cases} 1, & E - \Delta E < E_n < E \\ 0, & \text{otherwise} \end{cases}$$

Canonical Ensemble: By §4.3, the correct matrix elements are given by:

$$\hat{\rho} = \frac{1}{Z} e^{-\beta \hat{H}}$$

with $Z = \text{tr} \left(e^{-\beta \hat{H}} \right)$ being the canonical partition function. We can also write

$$\begin{aligned} Z &= \text{tr} \left(e^{-\beta \hat{H}} \right) \\ &= \sum_n \langle \varphi_n | e^{-\beta \hat{H}} | \varphi_n \rangle \\ &= \sum_n \langle \varphi_n | e^{-\beta E_n} | \varphi_n \rangle \\ &= \sum_n e^{-\beta E_n} \end{aligned}$$

Grand Canonical Ensemble: By §1.4.4:

$$\hat{\rho} = \frac{1}{Z} e^{-\beta(\hat{H} - \mu \hat{N})}$$

where \hat{N} is the number operator and

$$Z = \text{tr} \left(e^{-\beta(\hat{H} - \mu \hat{N})} \right)$$

is the grand partition function. We know that

$$\hat{H} |\varphi_{n,N}\rangle = E_n |\varphi_{n,N}\rangle, \quad \hat{N} |\varphi_{n,N}\rangle = N_n |\varphi_{n,N}\rangle$$

And thus we can write Z as:

$$\begin{aligned} Z &= \text{tr} \left(e^{-\beta(\hat{H} - \mu \hat{N})} \right) \\ &= \sum_{n,N} \langle \varphi_{n,N} | e^{-\beta(\hat{H} - \mu \hat{N})} | \varphi_{n,N} \rangle \\ &= \sum_{n,N} \langle \varphi_{n,N} | e^{-\beta(E_n - \mu N_n)} | \varphi_{n,N} \rangle \quad \text{since } [\hat{H}, \hat{N}] = 0 \\ &= \sum_{n,N} e^{-\beta(E_n - \mu N_n)} \end{aligned}$$

Remark 1: All thermodynamic quantities can be calculated from the partition function as before. In particular, in the canonical ensemble, we have

$$F = -k_B T \ln Z = -k_B T \ln \left[\text{tr} \left(e^{-\beta \hat{H}} \right) \right]$$

and in the grand canonical ensemble:

$$J = -k_B T \ln Z = -k_B T \ln \left[\text{tr} \left(e^{-\beta(\hat{H} - \mu \hat{N})} \right) \right]$$

Remark 2: Statistical mechanics, quantum or classical, then boils down to calculating partition functions.

1.5.3 Fermions and Bosons

Consider a quantum system consisting of N particles, which, for simplicity, we will take to be non-interacting. Let the single particle energy levels be denoted $\mathcal{E}(n = 0, 1, 2, \dots)$. Each of the corresponding eigenstates can be occupied by $0, 1, 2, \dots$ particles.

Postulate 1: Quantum particles come in two species: fermions and bosons. For fermions, at most one particle can occupy a given energy eigenstate, while any number of bosons can occupy any given energy eigenstate.

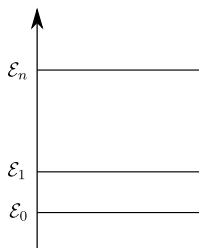
Remark 1: The restriction on fermions applies only to fermions of the same kind (eg, all electrons) whose quantum numbers are the same.

Remark 2: The fermionic restriction is known as the Pauli Exclusion Principle.

Remark 3: Fermions have half-integer spin, whereas bosons have integer spin.

1.5.4 The Fermi-Dirac Distribution

Consider a gas of N non-interacting fermions. Let the single particle spectrum be denoted $\{\mathcal{E}_n; n = 0, 1, \dots\}$, and consider the n th eigenstate (with energy \mathcal{E}_n) as the small subsystem under consideration.



The number of particles in a state is N_n , and thus the total energy of a subsystem is $\mathcal{E}_n N_n$. Also note that the system can exchange particles with other states, and thus the grand canonical ensemble is appropriate. Thus the partition function of the subsystem is:

$$\begin{aligned} Z_n &= \sum_{N_n} e^{\beta \mu N_n} e^{-\beta \mathcal{E}_n N_n} \\ &= \sum_{N_n} \left[e^{\beta(\mu - \mathcal{E}_n)} \right]^{N_n} \\ &= 1 + e^{\beta(\mu - \mathcal{E}_n)} \end{aligned}$$

since $N_n = \{0, 1\}$ for fermions. We also have that

$$\begin{aligned} J_n &= -k_B T \ln Z_n \\ &= -k_B T \ln \left[1 + e^{\beta(\mu - \mathcal{E}_n)} \right] \end{aligned}$$

which is the thermodynamic potential for the n th state.

Proposition 1: The grand canonical potential for a system of non-interacting fermions is:

$$J = -k_B T \sum_n \ln \left[1 + e^{\beta(\mu - \mathcal{E}_n)} \right]$$

Proof: $J = \sum_n J_n$

Theorem: The average number of fermions in the state with energy \mathcal{E} is given by

$$\langle N_n \rangle = \frac{1}{1 + e^{\beta(\mathcal{E}_n - \mu)}} := f_\mu(\mathcal{E}_n)$$

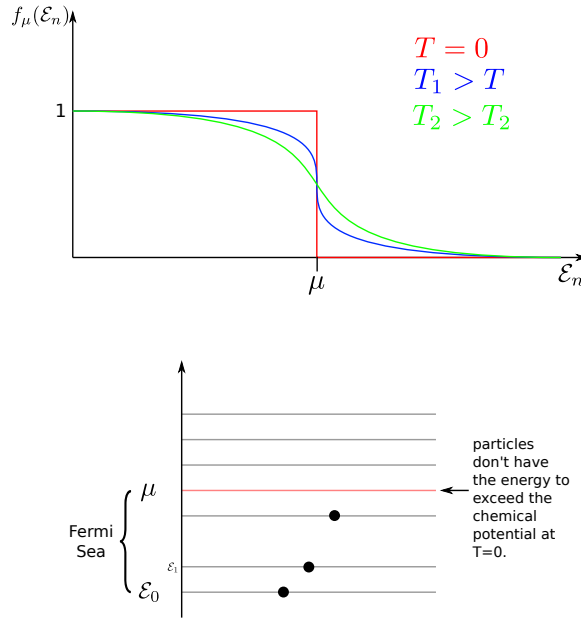
and the chemical potential μ is implicitly determined by the requirement

$$\begin{aligned} \sum_n f_n(\mathcal{E}_n) &= N \\ \Rightarrow \mu &= \mu(T, N) \end{aligned}$$

where N is the total number of fermions.

Proof: By §4.4.P2, we have that

$$\begin{aligned} \langle N_n \rangle &= - \left(\frac{\partial J_n}{\partial \mu} \right)_{T, V} \\ &= k_B T \left(\frac{\beta e^{\beta(\mu - \mathcal{E}_n)}}{1 + e^{\beta(\mu - \mathcal{E}_n)}} \right) \\ &= \frac{1}{e^{-\beta(\mu - \mathcal{E}_n)}} \\ &= \frac{1}{1 + e^{\beta(\mathcal{E}_n - \mu)}} \end{aligned}$$



Remark 1: $f_\mu(\mathcal{E}_n)$ is the Fermi-Dirac distribution, and has the following properties:

1. decreases monotonically with increasing energy
2. $f_\mu(\mathcal{E} = \mu) = \frac{1}{2}$
3. $f_\mu(\mathcal{E} \gg \mu) \rightarrow 0$
4. $f_\mu(\mathcal{E})|_{T=0} = \Theta(\mu(T=0) - \mathcal{E})$

Remark 2: $\mu(T=0) := \mathcal{E}_f$ is called the Fermi Energy.

1.5.5 The Bose-Einstein Distribution

Consider N non-interacting bosons. The partition function for the n th eigenstate is

$$Z_n = \sum_{N_n} \left(e^{\beta(\mu - \mathcal{E}_n)} \right)^{N_n}$$

Since bosons have $N_n = 0, 1, 2, \dots, \infty$, we have a geometric series.

$$\Rightarrow Z_n = \frac{1}{1 - e^{\beta(\mu - \mathcal{E}_n)}} \quad (\star)$$

$$\Rightarrow J_n = k_B T \ln \left(1 - e^{\beta(\mu - \mathcal{E}_n)} \right)$$

which is the thermodynamic potential for the n th state.

Proposition: The grand potential for a system of non-interacting bosons is:

$$J = k_B T \sum_n \ln \left[1 - e^{\beta(\mu - \mathcal{E}_n)} \right]$$

Theorem: The average number of bosons in the state with energy \mathcal{E}_n is:

$$\langle N_n \rangle = \frac{1}{e^{\beta(\mathcal{E}_n - \mu)} - 1} := n_\mu(\mathcal{E}_n)$$

and the chemical potential is implicitly determined by

$$\sum_n n_\mu(\mathcal{E}_n) = N \quad \Rightarrow \quad \mu = \mu(T, N)$$

Proof:

$$\begin{aligned} \langle N_n \rangle &= - \frac{\partial J_n}{\partial \mu} \\ &= k_B T \frac{e^{\beta(\mu - \mathcal{E}_n)} \beta}{1 - e^{\beta(\mu - \mathcal{E}_n)}} \\ &= \frac{1}{e^{\beta(\mathcal{E}_n - \mu)} - 1} \end{aligned}$$

Remark 1: $n_\mu(\mathcal{E})$ is called the Bose-Einstein distribution.

Remark 2: The geometric series (\star) must converge for all energies \mathcal{E}_n . In particular, for the ground state $\mathcal{E}_0 = 0 \Rightarrow e^{\beta\mu} < 1$. But $\beta = \frac{1}{k_B T} > 0 \Rightarrow \mu < 0$ for bosons. Thus, for bosons, the chemical potential is *always* negative. For fermions, the chemical potential can be either positive or negative (depends on temperature; for low temp, $\mu > 0$, see Fermi Sea).

Remark 3: For $e^{\beta(\mu - \mathcal{E}_n)} \ll 1$, both $f_\mu(\mathcal{E})$ and $n_\mu(\mathcal{E})$ approach a boltzmann distribution:

$$\left. \begin{matrix} f_\mu(\mathcal{E}) \\ n_\mu(\mathcal{E}) \end{matrix} \right\} = \frac{1}{e^{\beta(\mathcal{E}_n - \mu)} \pm 1} = \frac{e^{\beta(\mu - \mathcal{E}_n)}}{1 \pm e^{\beta(\mu - \mathcal{E}_n)}} \approx e^{\beta\mu} e^{-\beta\mathcal{E}_n}$$

Also, $\beta(\mu - \mathcal{E}_n) \ll 0$ and $\mathcal{E}_n \gg \mu$ since the energy of the state is higher than that of adding one additional particle. Thus the above can be further simplified to give:

$$\left. \begin{matrix} f_\mu(\mathcal{E}) \\ n_\mu(\mathcal{E}) \end{matrix} \right\} \approx e^{-\beta\mathcal{E}_n}$$

Chapter 2

Selected Applications

2.1 Classical Systems

2.1.1 The Classical Monatomic Ideal Gas

Recall that a classical gas has

$$\begin{aligned} E &= \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{x}_1, \dots, \mathbf{x}_n) \\ &= \text{kinetic} + \text{potential} \end{aligned}$$

Remark 1: All interactions between gas particles and between gas and external fields are contained in U .

Remark 2: Exclude charged particles in magnetic fields, so that U depends on positions only.

Remark 3: For an ideal gas, there are no particle-particle interactions, and thus $U = 0$ except for volume restrictions due to container walls.

$$U(\mathbf{x}_1, \dots, \mathbf{x}_n) = \begin{cases} 0 & \text{if } \mathbf{x}_i \in V \\ \infty & \text{otherwise} \end{cases}$$

From §4.3, we have an expression for our partition function:

$$\begin{aligned} Z &= \frac{1}{h^{3N} N!} \int d\mathbf{p}_1 d\mathbf{p}_2 \dots d\mathbf{p}_N \int d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N e^{-\beta E(\{\mathbf{p}_i\}, \{\mathbf{x}_i\})} \\ &= \frac{1}{h^{3N} N!} \underbrace{\int d\mathbf{p}_1 \dots d\mathbf{p}_N \exp \left[-\beta \sum_{i=1}^N \frac{1}{2m} \mathbf{p}_i^2 \right]}_{\text{integral over momentum only}} \cdot \underbrace{\int d\mathbf{x}_1 \dots d\mathbf{x}_N \exp [-\beta U(\mathbf{x}_1, \dots, \mathbf{x}_N)]}_{\text{integral over positions only}} \end{aligned}$$

In our case

$$U = \begin{cases} 0 \\ \infty \end{cases}$$

$$\begin{aligned} \Rightarrow Z &= \frac{1}{\hbar^{3N} N!} \left[d\mathbf{p} e^{-\beta p^2/2m} \right]^N V^N \\ &= \frac{V^N}{\hbar^{3N} N!} \left[4\pi \int_0^\infty dp p^2 e^{-\beta p^2/2m} \right]^N \end{aligned}$$

Let $p \rightarrow \sqrt{\frac{2m}{\beta}}$

$$\begin{aligned} &= \frac{V^N (4\pi)^N}{\hbar^{3N} N!} \left(\frac{2m}{\beta} \right)^{3N/2} \underbrace{\left[\int_0^\infty dx x^2 e^{-x^2} \right]}_{\frac{\sqrt{\pi}}{4}} \\ &= \frac{V^N (2mk_B T \pi)^{3N/2}}{\hbar^{3N} N!} \end{aligned}$$

Integral Trick: Let

$$\begin{aligned} I_\alpha &= \int_{-\infty}^\infty dx e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}} \\ \frac{dI}{d\alpha} &= - \int_{-\infty}^\infty dx x^2 e^{-\alpha x^2} = \frac{\sqrt{\pi}}{2} \end{aligned}$$

where $\alpha = 1$. Taking more derivatives can get you higher even powers of x .

Now, taking the natural log, we have that

$$\ln Z = N \ln V + \frac{3N}{2} \ln T + \frac{3N}{2} \ln \left(\frac{2\pi m k_B}{\hbar^2} \right) - \ln N!$$

We can use Stirlings approximation on the factorial to give us:

$$\begin{aligned} \ln Z &= N \ln V + \frac{3N}{2} \ln T + \frac{3N}{2} \ln \left(\frac{2\pi m k_B}{\hbar^2} \right) - N \ln N + N - \frac{1}{2} \ln(2\pi N) + \mathcal{O}\left(\frac{1}{N}\right) \\ &= N \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{2\pi m k_B}{\hbar^2} \right) + 1 + \mathcal{O}\left(\frac{1}{N} \ln N\right) \right] \end{aligned}$$

Remark 4: Within purely classical mechanics, one would write:

$$Z = \frac{1}{h_0^{3N}} \int \prod_i d\mathbf{p}_i \int \prod_j d\mathbf{x}_j e^{\beta E}$$

where h_0 is some quantity with dimensions of action. Choosing $h_0 = \hbar$ is a plausible quasi-classical choice, but the $\frac{1}{N!}$ is completely ad hoc. So we'll now look to see if this term makes a difference.

By Ch 1, §4.3:

$$p = k_B T = \frac{\partial \ln Z}{\partial V} = \frac{k_B T N}{V}$$

$$\Rightarrow pV = Nk_B T$$

So that works ok. What about the internal energy?

$$U = -\frac{\partial \ln Z}{\partial \beta} = \frac{3N}{2} \frac{1}{\beta} = \frac{3}{2} Nk_B T$$

So the internal energy is also fine. How about specific heat?

$$C_V = \frac{1}{\nu} \left(\frac{\partial U}{\partial T} \right) = \frac{3}{2} \frac{N}{\nu} k_B = \frac{3}{2} N_A k_B = \frac{3}{2} R$$

Still good!

Remark 5: None of the above results depend on the $\frac{1}{N!}$ prefactor.

Now, from Ch 1 §4.3, we have that

$$F = -k_B T \ln Z$$

$$\begin{aligned} S &= \frac{-\partial F}{\partial T} = k_B \ln Z + k_B T \frac{\partial \ln Z}{\partial T} \\ &= k_B \ln Z + k_B T \left(\frac{3N}{2T} \right) \\ &= \frac{3}{2} Nk_B + \underbrace{k_B \ln Z}_{\substack{\text{depends on} \\ \frac{1}{N!}}} \end{aligned}$$

$$S = k_B N \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln T \sigma_0 \right]$$

$$\text{where } \sigma_0 = \frac{5}{2} + \frac{3}{2} \ln \left(\frac{2\pi m k_B}{\hbar^2} \right)$$

Remark 6: So S does depend on the $\frac{1}{N!}$ prefactor.

2.1.2 The Gibbs Paradox

Suppose we had omitted the $\frac{1}{N!}$ prefactor. Then we would have a partition function:

$$\ln \tilde{Z} = N \left[\ln V + \frac{3}{2} \ln T + \tilde{\sigma}_0 - \frac{3}{2} \right]$$

where $\tilde{\sigma}_0 = \sigma_0 - 1$. The entropy in this case would then be:

$$\tilde{S} = Nk_B \left[\ln V + \frac{3}{2} \ln T + \tilde{\sigma}_0 \right]$$

There is something wrong with this expression though. To determine what, we will consider the thought experiment of Gibbs.

Assume we have an ideal gas with N particles in volume V . We insert a partition, creating two systems with $\frac{N}{2}$ particles in each $\frac{V}{2}$ volume.

Remark 1: This is a reversible process, and thus $S = S_1 + S_2$.

So now

$$\tilde{S} = Nk_B \left[\ln V + \frac{3}{2} \ln T + \tilde{\sigma}_0 \right]$$

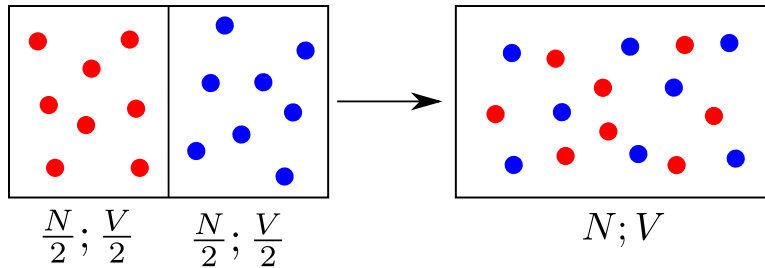
And thus

$$\begin{aligned} \tilde{S}_1 + \tilde{S}_2 &= 2\tilde{S}_1 = 2 \left(\frac{N}{2} \right) k_B \left[\ln \left(\frac{V}{2} \right) + \frac{3}{2} \ln T + \tilde{\sigma}_0 \right] \\ &= \tilde{S} - Nk_B \ln(2) \\ &< \tilde{S} \end{aligned}$$

But this is a violation of what really happens!!

Remark 2: This inconsistency of classical statistical mechanics is called the Gibbs's Paradox.

Consider instead a mixed system:



Remark 3: Suppose we painted the molecules in the left and right compartments red and blue, respectively, before removing the partition. The mixing of red and blue would be irreversible, and thus $\tilde{S} > \tilde{S}_1 + \tilde{S}_2$.

Remark 4: Thus, the paradox arises from the indistinguishability of the particles.

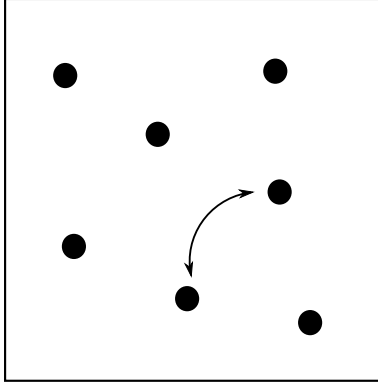


Figure 2.1: There are $N!$ ways to swap these particles, all of which contribute to only 1 microstate

So \tilde{Z} counts the microstates that arise from the $N!$ possible permutations of the particles of different microstates. This is correct for distinguishable particles, but wrong for indistinguishable ones. For indistinguishable particles, divide Z by $N!$ in order to get the correct partition function.

If we go back and include the $N!$ factors in the sum of the original entropies:

$$\begin{aligned} S_1 + S_2 &= 2S_1 = 2 \left(\frac{N}{2} \right) k_B \left[\ln \left(\frac{V/2}{N/2} \right) + \frac{3}{2} \ln T + \sigma_0 \right] \\ &= Nk_b \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln T + \sigma_0 \right] \\ &= S \end{aligned}$$

2.1.3 The Equipartition Theorem

Consider a classical system with $2f$ degrees of freedom and energy

$$E(\gamma) = E(p_1, p_2, \dots, p_f; q_1, q_2, \dots, q_f)$$

with f generalized coordinates q_i and f generalized momenta p_i .

Theorem: Let one degree of freedom (either p or q – without loss of generality, pick p_1) enter E quadratically, and let E be an arbitrary function of the remaining degrees

of freedom.

$$E = ap_1^2 + \mathcal{E}(p_2, \dots, p_f, q_1, \dots, q_f)$$

where a is a constant. Then p_1 contributes $\frac{1}{2}k_B T$ to the internal energy.

$$\langle ap_1^2 \rangle = \frac{1}{2}k_B T$$

Proof:

$$\begin{aligned} \langle ap_1^2 \rangle &= \frac{1}{Z} \int dq_1 dq_2 \dots dq_f dp_1 dp_2, \dots, dp_f ap_1^2 e^{-\beta E(\gamma)} \\ &= \frac{\int ap_1^2 e^{-\beta ap_1^2} dp_1 \int e^{-\beta \mathcal{E}(p_2 \dots p_f, q_1 \dots q_f)} dp_2 \dots dp_f dq_1 \dots dq_f}{\int e^{-\beta ap_1^2} dp_1 \int e^{-\beta \mathcal{E}(p_2 \dots p_f, q_1 \dots q_f)} dp_2 \dots dp_f dq_1 \dots dq_f} \end{aligned}$$

Let $p = \sqrt{a}p_1$

$$\begin{aligned} &= \frac{\int p^2 e^{-\beta p^2} dp}{\int e^{-\beta p^2} dp} \\ &= \frac{1}{2\beta} \\ &= \frac{1}{2}k_B T \end{aligned}$$

Remark 1: Every quadratic or harmonic degree of freedom contributes $\frac{1}{2}k_B T$ to the internal energy and $\frac{1}{2}R$ to the specific heat per mole.

Corollary: For a system with $2f$ degrees of freedom, all of which are harmonic, the internal energy and specific heat per mole are:

$$U = f k_B T$$

$$C_v = f R$$

which are collectively known as the “equipartition function”.

Remark 2: The equipartition theorem only holds classically.

Remark 3: Quantum mechanically, it holds to good approximation if $k_B T$ is large compared to typical spacing between energy levels.

Examples:

1. Consider a 1-d classical harmonic oscillator:

$$\begin{aligned} E &= \frac{p^2}{2m} + \frac{m}{2} \omega^2 q^2 \\ \Rightarrow U &= k_B T, \quad C_v = R \end{aligned}$$

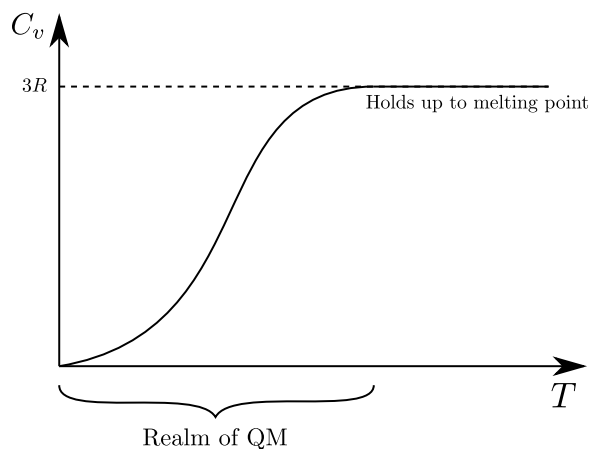
2. Consider instead a solid with N_A atoms/mole that is well modeled by N_A 3-d harmonic oscillators with energy:

$$E = \sum_{i=1}^{3N_A} \left(\frac{p_i^2}{2m_i} + \frac{m_i \omega_i^2 q_i^2}{2} \right)$$

where q_i are suitably chosen “normal coordinates”, and p_i are the corresponding conjugate momenta. Classically, one expects that

$$\frac{U}{\nu} = (2N_a) \frac{3}{2} k_B T = 3N_A k_B T$$

$$C_v = 3R \quad \leftarrow \text{“Law of Dulong and Petit”}$$



Remark 4: The Dulong-Petit law is well obeyed for high temperatures, where $T \geq \Theta_D$ where Θ_D is the Dulong temperature.

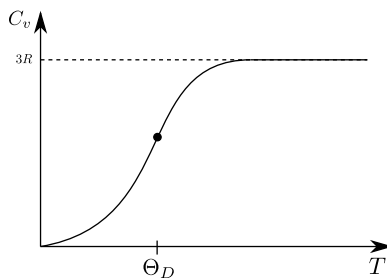


Figure 2.2: $\Theta_D \approx 100 - 400$ K for most materials.

For $T \ll \Theta_D$, $C_v \sim T^3$ (Debye’s Law, see solid state physics).

2.1.4 Maxwell's Velocity Distribution – Part I: Canonical Ensembles

Consider one molecule of a classical gas. The energy of the molecule is:

$$E = \frac{\mathbf{p}^2}{2m} + U(\mathbf{x}) = E(\mathbf{p}, \mathbf{x})$$

Remark 1: $U(\mathbf{x})$ is complicated since it depends on all other molecules.

Remark 2: Consider the molecule as the system, and the rest of the gas as the heat bath. Thus we have a canonical ensemble (this will be justified later in §2.1.5). Thus, the probability density for the molecule to be at point \mathbf{x} with momenta \mathbf{p} is:

$$\rho(\mathbf{x}, \mathbf{p}) \sim e^{\beta E(\mathbf{p}, \mathbf{x})}$$

Thus the probability density for the molecule to have a momenta \mathbf{p} irrespective of its position would be:

$$\begin{aligned} \rho(\mathbf{p}) &= \int \rho(\mathbf{p}, \mathbf{x}) d\mathbf{x} \sim e^{\beta \mathbf{p}^2/2m} \int e^{-\beta U(\mathbf{x})} \\ &= \mathcal{C} \cdot e^{-\beta \mathbf{p}^2/2m} \end{aligned}$$

Remark 3: No matter how complicated $U(\mathbf{x})$ is, $\int e^{-\beta U(\mathbf{x})} d\mathbf{x}$ can depend only on β .

Normalizing:

$$\begin{aligned} 1 &= \int \rho(\mathbf{p}) d\mathbf{p} = \mathcal{C} \int e^{-\beta \mathbf{p}^2/2m} d\mathbf{p} \\ &= \mathcal{C}(4\pi) \int_0^\infty p^2 e^{-\beta p^2/2m} dp \\ &= \mathcal{C}(4\pi) \left(\frac{2m}{\beta}\right)^{3/2} \underbrace{\int_0^\infty x^2 e^{-x^2} dx}_{\frac{\sqrt{\pi}}{4}} \\ &= \mathcal{C}(2\pi m k_B T)^{3/2} \\ &\Rightarrow \mathcal{C} = (2\pi m k_B T)^{-3/2} \\ &\Rightarrow \rho(\mathbf{p}) = \frac{1}{(2\pi m k_B T)^{3/2}} e^{-\beta \mathbf{p}^2/2m} = \text{momentum distribution} \end{aligned}$$

Now our goal is to determine the distribution for the velocity modulus $v = |\mathbf{v}| = \frac{1}{m}|\mathbf{p}|$. We know that probability is conserved, and thus:

$$\begin{aligned} \rho(\mathbf{v}) d\mathbf{v} &= \rho(\mathbf{p}) d\mathbf{p} \\ &= \rho(\mathbf{p} = m\mathbf{v}) dp_x dp_y dp_z \\ &= m^3 \rho(\mathbf{p} = m\mathbf{v}) dv_x dv_y dv_z \\ &= m^3 \rho(\mathbf{p} = m\mathbf{v}) d\mathbf{v} \end{aligned}$$

$$\Rightarrow \rho(\mathbf{v}) = m^3 \rho(\mathbf{p} = m\mathbf{v})$$

And

$$\begin{aligned} \rho(\mathbf{v}) &= \int \rho(\mathbf{v}) v^2 dv d\Omega \\ &= 4\pi v^2 \rho(\mathbf{v}) \\ &= 4\pi m^3 v^2 \rho(\mathbf{p} = m\mathbf{v}) \end{aligned}$$

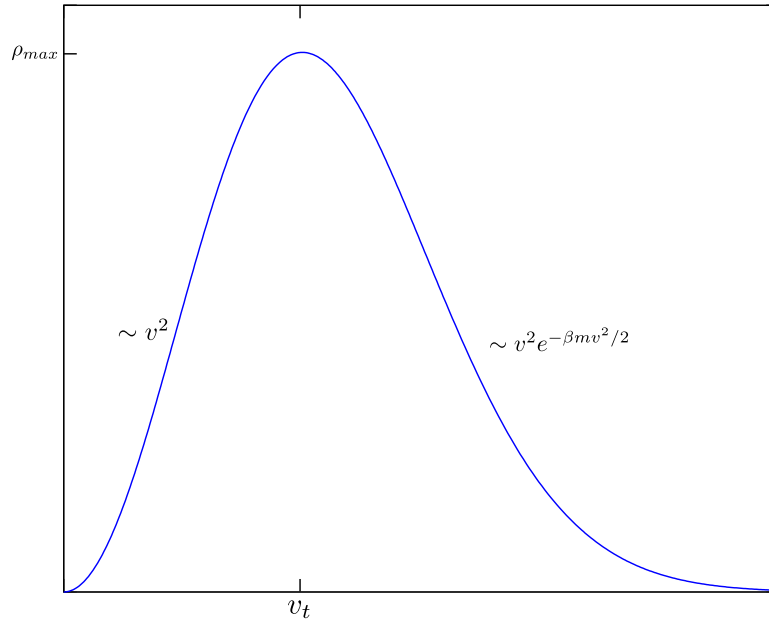
$$\Rightarrow \rho(\mathbf{v}) d\mathbf{v} = \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\beta m v^2 / 2}$$

is Maxwell's velocity distribution.

Remark 4: $\rho(\mathbf{v})$ is isotropic so it makes sense to consider $\rho(v)$.

Remark 5: Watch your Jacobians while changing variables. Probabilities (*NOT* probability densities) must be equal.

Discussion:



where v_t is the most probable (typical) velocity. Consider now the values of the different velocity measures:

1.

$$\begin{aligned} \rho(v \rightarrow 0) &\sim v^2 \\ \rho(v \rightarrow \infty) &\sim v^2 e^{-\beta m v^2 / 2} \end{aligned}$$

2. Mean velocity:

$$\begin{aligned}
 \langle v \rangle &= \int v \rho(v) dv \\
 &= 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \left(\frac{2k_B T}{m} \right)^{4/2} \int_0^\infty x^3 e^{-x^2} dx \\
 &= \frac{4}{\sqrt{\pi}} \left(\frac{2k_B T}{m} \right)^{1/2} \left[\frac{1}{2} \int_0^\infty y e^{-y} dy \right] \\
 &= \left(\frac{k_B T}{m} \right)^{1/2} \sqrt{\frac{8}{\pi}}
 \end{aligned}$$

3. RMS Velocity:

$$\begin{aligned}
 v_{rms} = \langle v^2 \rangle^{1/2} &= \left[4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty v^4 e^{-\beta v^2 m/2} dv \right]^{1/2} \\
 &= \left[\frac{4\pi}{\pi^{3/2}} \left(\frac{m}{2k_B T} \right)^{3/2} \left(\frac{2k_B T}{m} \right)^{5/2} \int_0^\infty x^4 e^{-x^2} dx \right]^{1/2} \\
 &= \left[\frac{4\pi}{\pi^{3/2}} \frac{3\pi^{1/2}}{8} \left(\frac{2k_B T}{m} \right) \right]^{1/2} \\
 &= \sqrt{3} \left(\frac{k_B T}{m} \right)^{1/2}
 \end{aligned}$$

4. Typical Velocity:

$$\begin{aligned}
 v_t = \left. \frac{\partial \rho}{\partial v} \right|_{v_t} = 0 &= 2v e^{-v^2 m/2k_B T} - v^2 \left(\frac{2mv}{2k_B T} \right) e^{-v^2 m/2k_B T} \\
 &\Rightarrow v_t = \sqrt{2} \left(\frac{k_B T}{m} \right)^{1/2} \\
 &\Rightarrow v_{rms} : \langle v \rangle : v_t = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} = 1.2225 : 1.128 : 1
 \end{aligned}$$

5. Standard Deviation:

$$\begin{aligned}
 \sigma &= \left(\langle v^2 \rangle - \langle v \rangle^2 \right)^{1/2} \\
 &= \left(\frac{k_B T}{m} \right)^{1/2} \left(3 - \frac{8}{\pi} \right)^{1/2} = 0.67 \left(\frac{k_B T}{m} \right)^{1/2}
 \end{aligned}$$

6. Relative Flucuation:

$$\frac{\sigma}{\langle v \rangle} = 0.422$$

And thus we do *not* have a sharply peaked distribution!

There is only one energy scale (thermal). So dimensionally:

$$E \sim mv^2$$

$$(k_B T) \sim mv^2 \quad \Rightarrow \quad v = \mathcal{C} \left(\frac{k_B T}{m} \right)^{1/2}$$

Remark 6: So $\langle v \rangle, v_t, v_{rms}$ all must be some number times $\left(\frac{k_B T}{m} \right)^{1/2}$ by dimensional analysis. $k_B T$ is the only energy scale in the problem, and $\left(\frac{k_B T}{m} \right)^{1/2}$ is the only velocity one can construct from that.

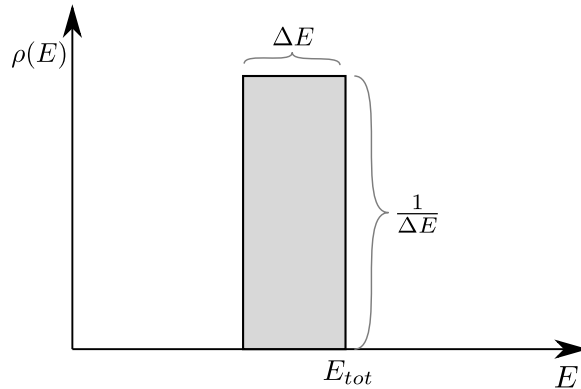
Remark 7: For N_2 , ($m = 2 \cdot 14 \cdot 1.6 \times 10^{-27}$ kg) at $T = 300$ K, we have that

$$\begin{aligned} \sqrt{\frac{k_B T}{m}} &= \left(\frac{1.38 \times 10^{-24} \cdot 300}{2 \cdot 14 \cdot 1.6 \times 10^{-27}} \right) \\ &\approx 300 \text{ m/s} \\ &\approx \text{speed of sound} \end{aligned}$$

2.1.5 Maxwell's Velocity Distribution – Part II: Microcanonical Ensemble

Consider an *isolated* classical gas, N particles in a volume V , and thus a microcanonical ensemble applies. By §1.4.2, we know that

$$\rho(E) = \frac{1}{\Delta E} \cdot \begin{cases} 1 & \text{if } E_{tot} - \Delta E < E < E_{tot} \\ 0 & \text{otherwise} \end{cases}$$



If we let $\Delta E \rightarrow 0$, then $\rho(E) = \delta(E - E_{tot})$.

Remark 1: The delta function reflects energy conservation.

We will define

$$\mathcal{E} := \frac{E_{tot}}{N}$$

to be the total energy per particle. Then, considering an ideal gas for simplicity, we have that

$$E(p, q) = \sum_{i=1}^N \frac{p_i^2}{2m}$$

What then is the probability density for a particle to be at some point in phase space (p, q) ?

$$\begin{aligned} \rho(p, q) &= A_N \delta(E(p, q) - N\mathcal{E}) \\ &= A_N \delta\left(\sum_{i=1}^N \frac{p_i^2}{2m} - N\mathcal{E}\right) \end{aligned}$$

where A_N is the normalization constant. Now, define

$$\begin{aligned} I_N(N\mathcal{E}) &:= \int d\mathbf{p}_1 d\mathbf{p}_2 \dots d\mathbf{p}_N \int d\mathbf{x}_1 d\mathbf{x}_2 \dots d\mathbf{x}_N \delta\left(\frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} + \dots + \frac{\mathbf{p}_N^2}{2m} - N\mathcal{E}\right) \\ &= V^N \int \delta\left(\frac{p_{1x}^2}{2m} + \frac{p_{1y}^2}{2m} + \frac{p_{1z}^2}{2m} + \dots + \frac{p_{Nx}^2}{2m} + \frac{p_{Ny}^2}{2m} + \frac{p_{Nz}^2}{2m} - N\mathcal{E}\right) dp_{1x} dp_{1y} dp_{1z} \dots dp_{Nx} dp_{Ny} dp_{Nz} \end{aligned}$$

Let

$$\begin{aligned} \mathbf{p} &= (p_{1x}, p_{1y}, p_{1z}, \dots, p_{Nx}, p_{Ny}, p_{Nz}) \\ \Rightarrow I_N(N\mathcal{E}) &= V^N \int \delta\left(\frac{1}{2m} (\mathbf{p} \cdot \mathbf{p}) - N\mathcal{E}\right) d^{3N}p \end{aligned}$$

Since

$$\delta(f(x)) = \sum_i \frac{1}{\left|\frac{\partial f}{\partial x}(x_i)\right|} \delta(x - x_i)$$

then

$$\begin{aligned} I_N(N\mathcal{E}) &= 2mV^N \int \delta(p^2 - 2mN\mathcal{E}) d^{3N}p \\ &= 2mV^N S_{3N} \int_0^\infty p^{3N-1} \delta(p^2 - 2mN\mathcal{E}) dp \end{aligned}$$

where S_{3N} is the surface of a $3N - 1$ unit sphere. Letting $x = p^2$:

$$\begin{aligned} I_N(N\mathcal{E}) &= 2mV^N S_{3N} \frac{1}{2} \int_0^\infty x^{(3N-2)/2} \delta(x - 2mN\mathcal{E}) dx \\ &= mV^N S_{3N} (2mN\mathcal{E})^{(3N-2)/2} \\ &= V^N (2m)^{3N/2} \frac{1}{2} S_{3N} (N\mathcal{E})^{\frac{3N}{2}-1} \end{aligned}$$

Now, by normalization:

$$1 = \int \rho(p, q) dp dq = A_N I_N(N\mathcal{E})$$

$$\Rightarrow A_N = \frac{1}{I_N(N\mathcal{E})}$$

Now consider particle 1. What is the probability density for particle 1 to be at point x with momentum p , irrespective of the other particles?

$$\begin{aligned} \rho^{(1)}(\mathbf{p}_1, \mathbf{x}_1) &= \int d\mathbf{p}_2 \dots d\mathbf{p}_N \int d\mathbf{x}_2 \dots d\mathbf{x}_N \rho(p, q) \\ &= A_N \int d\mathbf{p}_2 \dots d\mathbf{p}_N \int d\mathbf{x}_2 \dots d\mathbf{x}_N \delta\left(\frac{\mathbf{p}_2^2}{2m} + \dots + \frac{\mathbf{p}_N^2}{2m} - \left(N\mathcal{E} - \frac{\mathbf{p}_1^2}{2m}\right)\right) \\ &= \underbrace{A_N I_{N-1}}_{\frac{I_{N-1}}{I_N}} \left(N\mathcal{E} - \frac{\mathbf{p}_1^2}{2m}\right) \Theta\left(N\mathcal{E} - \frac{\mathbf{p}_1^2}{2m}\right) \end{aligned}$$

where the Θ function is a statement that the energy of \mathbf{p}_1 can't exceed the total energy.

$$\begin{aligned} \Rightarrow \rho^{(1)}(\mathbf{p}_1, \mathbf{x}_1) &= \frac{V^{N-1} (2m)^{3(N-1)/2} \frac{1}{2} \left(N\mathcal{E} - \frac{\mathbf{p}_1^2}{2m}\right)^{(3N-5)/2} \Theta\left(N\mathcal{E} - \frac{\mathbf{p}_1^2}{2m}\right) S_{3(N-1)}}{V^N (2m)^{3N/2} \frac{1}{2} S_{3N} (N\mathcal{E})^{(3N-2)/2}} \\ &= \frac{1}{V(2m)^{3/2}} \frac{S_{3(N-1)}}{S_{3N}} \frac{1}{(N\mathcal{E})^{3/2}} \left(1 - \frac{\mathbf{p}_1^2}{2mN\mathcal{E}}\right)^{(3N-5)/2} \Theta\left(N\mathcal{E} - \frac{\mathbf{p}_1^2}{2m}\right) \end{aligned}$$

Now we'll take the thermodynamic limit, recalling that $S_d = \frac{2\pi^{d/2}}{\Gamma(d/2)}$.

$$\begin{aligned} \lim_{N \rightarrow \infty} \frac{S_N}{S_{N-1}} &= \lim_{N \rightarrow \infty} \frac{2\pi^{N/2}}{\gamma(N/2)} \frac{\Gamma\left(\frac{N-1}{2}\right)}{2\pi^{(N-1)/2}} \\ &= \lim_{N \rightarrow \infty} \frac{\sqrt{\pi}}{\Gamma(N/2)} \frac{\sqrt{\pi}\Gamma(N-1)}{2^{N-2}\Gamma(N/2)} \\ &= \lim_{N \rightarrow \infty} \frac{\pi(N-2)!}{2^{N-2} \left(\left(\frac{N}{2} - 1\right)!\right)^2} \end{aligned}$$

By the Stirling approximation:

$$\begin{aligned} &= \pi \lim_{N \rightarrow \infty} \frac{(N-2)^{N-2} e^{-(N-2)} \sqrt{2\pi(N-2)}}{2^{N-2} \left(\frac{N-2}{2}\right)^{N-2} e^{-(N-2)} 2\pi \left(\frac{N-2}{2}\right)} \left[1 + \mathcal{O}\left(\frac{1}{N}\right)\right] \\ &= \lim_{N \rightarrow \infty} \sqrt{\frac{2\pi}{N-2}} \left[1 + \mathcal{O}\left(\frac{1}{N}\right)\right] \\ &= \lim_{N \rightarrow \infty} \sqrt{\frac{2\pi}{N}} \left[1 + \mathcal{O}\left(\frac{1}{N}\right)\right] \end{aligned}$$

Now, looking at

$$\begin{aligned} \lim_{N \rightarrow \infty} \left(1 - \frac{a}{N}\right)^{bN+c} &= \lim_{N \rightarrow \infty} \underbrace{\exp \left[(bN+c) \ln \left(1 - \frac{a}{N}\right) \right]}_{\exp \left[(bN+c) \left(-\frac{a}{N} + \frac{1}{N^2}\right) \right]} \\ &= e^{-ab} \left[1 + \mathcal{O} \left(\frac{1}{N} \right) \right] \end{aligned}$$

So

$$\begin{aligned} \rho^{(1)}(\mathbf{p}, \mathbf{x}) &= \frac{(2\pi)^{-3/2}}{V} \frac{S_{3N-3}}{S_{3N-2}} \frac{S_{3N-2}}{S_{3N-1}} \frac{S_{3N-1}}{S_{3N}} \frac{1}{(N\mathcal{E})^{3/2}} \left(1 - \frac{\mathbf{p}^2/2m\mathcal{E}}{N}\right)^{\frac{3N}{2} - \frac{5}{2}} \Theta \left(N\mathcal{E} - \frac{\mathbf{p}^2}{2m} \right) \\ \Rightarrow \lim_{N \rightarrow \infty} \rho^{(1)}(\mathbf{p}, \mathbf{x}) &= \frac{1}{V} \frac{1}{(2mN\mathcal{E})^{3/2}} \left(\frac{3N}{2\pi} \right)^{3/2} e^{-\frac{3}{2} \frac{\mathbf{p}^2}{2m\mathcal{E}}} \left[1 + \mathcal{O} \left(\frac{1}{N} \right) \right] \end{aligned}$$

Define

$$k_B\theta := \frac{2\mathcal{E}}{3}$$

Then

$$\rho^{(1)}(\mathbf{p}, \mathbf{x}) = \frac{1}{V} \frac{1}{(2\pi m k_B \theta)^{3/2}} \exp \left[-\frac{\mathbf{p}^2}{2m k_B \theta} \right] \left[1 + \mathcal{O} \left(\frac{1}{N} \right) \right]$$

We can then integrate over x if we want to get the momentum distribution.

Remark 2: This is again the Maxwell distribution with $\beta = \frac{1}{k_B\theta}$, where θ is the microcanonical “temperature”.

Remark 3: In the microcanonical ensemble, energy is the fundamental variable, and thus temperature is defined in terms of total energy per particle.

Now consider the probability distribution for 2 particles:

$$\begin{aligned} \rho^{(2)}(\mathbf{p}_1, \mathbf{x}_1, \mathbf{p}_2, \mathbf{x}_2) &= \int d\mathbf{p}_3 \dots d\mathbf{p}_N \int d\mathbf{x}_3 \dots d\mathbf{x}_N \rho(\mathbf{p}, \mathbf{q}) \\ &= A_N \Theta \left(N\mathcal{E} - \left(\frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} \right) \right) I_{N-2} \left(N\mathcal{E} - \frac{1}{2m} (\mathbf{p}_1^2 + \mathbf{p}_2^2) \right) \\ &= \Theta \left(N\mathcal{E} - \left(\frac{\mathbf{p}_1^2}{2m} + \frac{\mathbf{p}_2^2}{2m} \right) \right) \frac{2m^{-3}}{V^2} \frac{S_{3N-6}}{S_{3N}} \frac{1}{(N\mathcal{E})^3} \left[1 - \frac{(\mathbf{p}_1^2 + \mathbf{p}_2^2)}{2mN\mathcal{E}} \right]^{\frac{3N}{2} - \frac{8}{2}} \\ \lim_{N \rightarrow \infty} \rho^{(2)} &= \frac{(2m)^{-3}}{V} \left(\frac{3N}{2\pi} \right)^3 \exp \left[-\frac{3}{2} \frac{(\mathbf{p}_1^2 + \mathbf{p}_2^2)}{2m\mathcal{E}} \right] \frac{1}{(N\mathcal{E})^3} \left[1 + \mathcal{O} \left(\frac{1}{N} \right) \right] \\ &= \rho^{(1)}(\mathbf{p}_1, \mathbf{x}_1) \rho^{(1)}(\mathbf{p}_2, \mathbf{x}_2) \left[1 + \mathcal{O} \left(\frac{1}{N} \right) \right] \end{aligned}$$

Remark 4: $N \rightarrow \infty$ simplifies calculations!

Remark 5: In the thermodynamic limit, the particles become statistically independent. This justifies the canonical treatment, where we were treating 1 particle as the system and the rest as a heat bath.

2.2 The Ideal Fermi Gas

2.2.1 Distribution Functions and the Equation of State for Fermions and Bosons

We want to look at an ideal quantum gas (fermions or bosons) where we will characterize single particle energy states by the momenta \mathbf{p} .

$$\mathcal{E}_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m}$$

The phase space volume, $d\gamma$ gives

$$\frac{d\gamma}{(2\pi\hbar)^3} = \frac{d\mathbf{p} d\mathbf{x}}{(2\pi\hbar)^3}$$

The number of particles in a particular phase space volume is:

$$dN = \underbrace{\langle N_{\mathbf{p}} \rangle}_{\substack{\# \text{ particles} \\ \text{per state}}} \cdot \underbrace{\frac{d\gamma}{(2\pi\hbar)^3}}_{\substack{\text{states per} \\ \text{volume}}} = \frac{1}{e^{\beta(\mathcal{E}_{\mathbf{p}} - \mu)} \pm 1} \cdot \frac{d\mathbf{p} d\mathbf{x}}{(2\pi\hbar)^3}$$

Remark 1: The upper sign is for fermions, the lower for bosons.

Remark 2: For particles with spin S , there are $2S + 1 = g$ possible values of spin projection. Thus all energy eigenstates are g -fold degenerate.

$$\Rightarrow dN = \frac{g}{(2\pi\hbar)^3} \frac{d\mathbf{p} d\mathbf{x}}{\exp[\beta(\mathcal{E}_{\mathbf{p}} - \mu)] \pm 1}$$

The number of particles with momenta between \mathbf{p} and $\mathbf{p} + d\mathbf{p}$ is

$$dN_{\mathbf{p}} = \int_V dN d\mathbf{x} = \frac{gV}{(2\pi\hbar)^3} \frac{d\mathbf{p}}{e^{\beta(\mathcal{E}_{\mathbf{p}} - \mu)} \pm 1}$$

And the number of particles with $p = |\mathbf{p}|$ between p and $p + dp$:

$$dN_p = \frac{4\pi gV}{(2\pi\hbar)^3} \frac{p^2 dp}{e^{\beta(\mathcal{E}_p - \mu)} \pm 1} \quad (\star)$$

where $\mathcal{E}_p = \frac{p^2}{2m}$. This is the distribution function for the modulus of the momentum for an ideal Fermi or Bose gas.

Remark 3: (\star) is the quantum mechanical analog of the Maxwell distribution, §1.1.4.

Let's now switch from momentum to energy:

$$\begin{aligned}\mathcal{E} = \frac{p^2}{2m} &\Rightarrow d\mathcal{E} = \frac{p}{m} dp \\ \Rightarrow dp = \frac{m}{p} d\mathcal{E} &= \frac{m}{\sqrt{2m\mathcal{E}}} d\mathcal{E}\end{aligned}$$

By conservation of probability:

$$\begin{aligned}\rho(p) dp &= \rho(\mathcal{E}) d\mathcal{E} \\ &= \rho(\mathcal{E}) \frac{1}{m} \frac{\sqrt{2m\mathcal{E}}}{m} dp \\ \Rightarrow \rho(\mathcal{E}) &= \frac{m}{\sqrt{2m\mathcal{E}}} \rho(p = \sqrt{2m\mathcal{E}}) \\ &= \frac{m}{\sqrt{2m\mathcal{E}}} \frac{gV}{2\pi^2 \hbar^3} \frac{2m\mathcal{E}}{e^{\beta(\mathcal{E}-\mu)} \pm 1} \\ &= \frac{gVm^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \frac{\mathcal{E}^{1/2}}{e^{\beta(\mathcal{E}-\mu)} \pm 1}\end{aligned}$$

Remark 4: $\rho(\mathcal{E}) d\mathcal{E}$ equals the number of particles with energy \mathcal{E} ($[\mathcal{E}, \mathcal{E} + d\mathcal{E}]$).

$$\begin{aligned}\Rightarrow N &= \int_0^\infty \rho(\mathcal{E}) d\mathcal{E} \\ &= \frac{gVm^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\mathcal{E}^{1/2}}{e^{\beta(\mathcal{E}-\mu)} \pm 1} d\mathcal{E} \\ &= \int_0^\infty \rho(p) dp \\ &= \frac{gV}{2\pi^2 \hbar^3} \int_0^\infty \frac{p^2}{e^{\beta(\mathcal{E}_n-\mu)} \pm 1} dp \\ &= \sum_n \left[\frac{f_\mu(\mathcal{E}_n)}{n_\mu(\mathcal{E}_n)} \right] \\ &= \sum_n \frac{1}{e^{\beta(\mathcal{E}_n-\mu)} \pm 1}\end{aligned}$$

Thus the transition from discrete quantum states to continuous ones is accompanied by taking the limit:

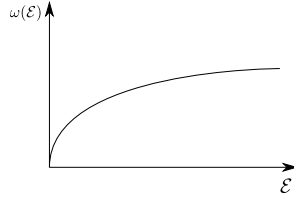
$$\sum_n \rightarrow \frac{gVm^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \sqrt{\mathcal{E}} d\mathcal{E}$$

or

$$\sum_n \rightarrow \frac{gV}{2\pi^2\hbar^3} \int_0^\infty p^2 dp$$

Remark 5: The density of states(DoS) per unit volume, $\omega(\mathcal{E})$, is determined by:

$$\begin{aligned} n &= \frac{N}{V} = \int_0^\infty \omega(\mathcal{E}) d\mathcal{E} \left\{ \frac{f_\mu(\mathcal{E})}{n_\mu(\mathcal{E})} \right\} \\ \frac{1}{V} \sum_n \left\{ \frac{f_\mu(\mathcal{E})}{n_\mu(\mathcal{E})} \right\} &\rightarrow \frac{gm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \sqrt{\mathcal{E}} \left\{ \frac{f_\mu(\mathcal{E})}{n_\mu(\mathcal{E})} \right\} d\mathcal{E} \\ \Rightarrow \omega(\mathcal{E}) &= \frac{gm^{3/2}\sqrt{\mathcal{E}}}{\sqrt{2}\pi^2\hbar^3} \Theta(\mathcal{E}) \end{aligned}$$



Remark 6: Alternatively, one can derive the density of states by “fitting waves into boxes”. Consider a quantum mechanical particle confined in a 3d cube of length L . The wave function is:

$$\psi \sim \sin\left(\frac{2\pi n_x x}{L}\right) \sin\left(\frac{2\pi n_y y}{L}\right) \sin\left(\frac{2\pi n_z z}{L}\right)$$

where

$$\begin{aligned} n_{x,y,z} &= \text{the number of waves fitting into the box} \\ \Rightarrow \mathbf{k} &= \frac{2\pi}{L} (n_x, n_y, n_z) \end{aligned}$$

The number of states with \mathbf{k} between \mathbf{k} and $\mathbf{k} + d\mathbf{k}$ is given by

$$\left(\frac{L}{2\pi}\right)^3 dk_x dk_y dk_z$$

So the density of states is:

$$\omega(\mathbf{k}) d\mathbf{k} = \frac{V dk_x dk_y dk_z}{(2\pi)^3} \cdot g$$

$$\omega(\mathbf{k}) d\mathbf{k} = \omega(\mathbf{p}) d\mathbf{p} = \frac{V dp_x dp_y dp_z \cdot g}{(2\pi\hbar)^3}$$

Which gives

$$\begin{aligned} \omega(p) dp &= \frac{4\pi V g p^2 dp}{(2\pi\hbar)^3} = \omega(\mathcal{E}) d\mathcal{E} \\ &= \frac{4\pi V g}{(2\pi\hbar)^3} (2m\mathcal{E}) \sqrt{\frac{m}{2\mathcal{E}}} d\mathcal{E} \\ \Rightarrow \omega(\mathcal{E}) &= \frac{V g m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \mathcal{E}^{1/2} \end{aligned}$$

Before we wrote the density of states per volume, so it was already divided by V .

Recall from §1.4.3.R2 that

$$Z = \int_0^\infty \omega(\mathcal{E}) e^{-\beta\mathcal{E}} d\mathcal{E}$$

which applied either classically or quantum mechanically. Thus, for us to determine the equation of state for a quantum mechanical gas, we need to find J . By §1.5.4 and §1.5.5, we have that

$$J = \mp k_B T \sum_n \ln \left[1 \pm e^{\beta(\mu - \mathcal{E}_n)} \right]$$

And in the thermodynamic limit,

$$J = \mp k_B T \frac{g V m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \mathcal{E}^{1/2} \ln \left[1 \pm e^{\beta(\mu - \mathcal{E})} \right] d\mathcal{E} \quad (\star)$$

Proposition: The grand canonical thermodynamic potential J of an ideal quantum gas is:

$$J = \frac{-\frac{2}{3} g V m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\mathcal{E}^{3/2}}{e^{\beta(\mathcal{E} - \mu)} \pm 1} d\mathcal{E}$$

Proof: We integrate (\star) by parts, with $dv = \sqrt{\mathcal{E}} d\mathcal{E}$, $u = \ln [1 \pm e^{\beta(\mu - \mathcal{E})}]$:

$$\begin{aligned} J &= \frac{\mp k_B T g V m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} - \int_0^\infty \frac{2}{3} \mathcal{E}^{3/2} \frac{\pm e^{\beta(\mu - \mathcal{E})} \left(-\frac{1}{k_B T}\right)}{1 \pm e^{\beta(\mu - \mathcal{E})}} + \text{stuff} \left(\mathcal{E}^{3/2} \ln [1 \pm e^{\beta(\mu - \mathcal{E})}] \right) \\ &= \frac{-\frac{2}{3} g V m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\mathcal{E}^{3/2}}{e^{\beta(\mathcal{E} - \mu)} \pm 1} d\mathcal{E} \end{aligned}$$

Corollary: The equation of state for an ideal quantum gas (in 3d) is:

$$PV = \frac{2}{3} U(N, T)$$

Proof: By §1.4.4, we know that $J = -PV$:

$$U = \int_0^\infty \mathcal{E} \rho(\mathcal{E}) d\mathcal{E} = \frac{gV m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\mathcal{E}^{3/2}}{e^{\beta(\mathcal{E}-\mu)} \pm 1} = \frac{-3}{2} J = \frac{3}{2} PV$$

Remark 7: Since this is completely general, it must hold in the classical limit. By §1.1:

$$U = N \frac{3}{2} k_B T$$

$$\Rightarrow PV = N k_B T = \frac{2}{3} U$$

However, this is only true in 3d!

2.2.2 The Degenerate Gas

Consider a Fermi gas at $T = 0$ (the “completely degenerate case”). By §1.5.4, the particle number can be given by:

$$\begin{aligned} N &= \sum_p \langle N_p \rangle = \sum_p \frac{1}{e^{\beta(\mathcal{E}_p - \mu)} + 1} = \sum_p \Theta(\mu - \mathcal{E}_p) \\ &= \frac{gV m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \sqrt{\mathcal{E}} \Theta(\mathcal{E}_F - \mathcal{E}) d\mathcal{E} \\ &= \frac{2V m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \sqrt{\mathcal{E}} d\mathcal{E} \\ &= \frac{2V m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \frac{2}{3} \mathcal{E}_F^{3/2} \end{aligned}$$

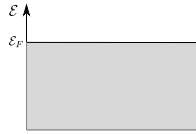


Figure 2.3: The shaded region is the energies filled to \mathcal{E}_F , which depends on the number of particles.

Thus the Fermi energy in terms of the density is

$$\mathcal{E}_F = \frac{(3\pi^2)^{2/3}}{2m} \hbar^2 n^{2/3}$$

Definition 1: The Fermi momentum p_F , is defined by:

$$\mathcal{E}_F := \frac{p_F^2}{2m}$$

And the Fermi wave-number k_F is $\hbar k_F = p_F$.

$$\Rightarrow p_F = \sqrt{2m\mathcal{E}_F} = (3\pi^2)^{1/3} \hbar n^{1/3}$$

From §2.1, we know that the pressure is:

$$\begin{aligned} P &= \frac{2}{3V} U = \frac{2}{3V} \frac{2Vm^{3/2}}{\sqrt{2\pi^2\hbar^3}} \int_0^\infty \mathcal{E}^{3/2} \Theta(\mathcal{E}_F - \mathcal{E}) d\mathcal{E} \\ &= \frac{4}{3} \frac{m^{3/2}}{\sqrt{2\pi^2\hbar^3}} \frac{2}{5} \mathcal{E}_F^{5/2} \\ &= \frac{8}{15} \frac{m^{3/2}}{\sqrt{2\pi^2\hbar^3}} \left[\frac{(3\pi^2)^{5/3} \hbar^5}{(2m)^{5/2}} n^{5/3} \right] \\ &= \frac{1}{5} \frac{\hbar^2}{m} (3\pi^2)^{2/3} n^{5/3} \\ &= \text{pressure in terms of density} \end{aligned}$$

Remark 1: $P \sim n^{5/2}$ as opposed to $P \sim n$ in a classical gas.

Remark 2: The gas is degenerate for $T \ll \frac{\mathcal{E}_F}{k_B} := T_F$, where T_F is the Fermi temperature.

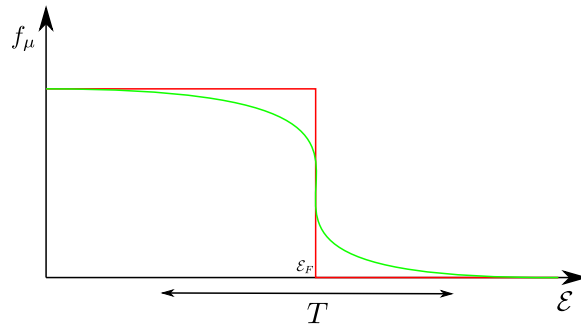
Remark 3: Important Applications: electrons in metals

$$\mathcal{E}_F \sim 10 \text{ eV} \quad \Rightarrow \quad 100000 \text{ K}$$

Remark 4: Other important applications: He^3 , white dwarfs, neutron stars.

2.2.3 The Specific Heat of a Degenerate Electron Gas

We will be considering low temperatures: $0 < T \ll T_F$



By §2.1:

$$J = -\frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} I(\mu, T)$$

$$I(\mu, T) = \int_0^\infty \frac{\mathcal{E}^{3/2}}{e^{\beta(\mathcal{E}-\mu)} + 1}$$

Let $k_B = 1$, $z = \frac{\mathcal{E}-\mu}{T}$, $dz = \frac{1}{T} d\mathcal{E}$:

$$\begin{aligned} \Rightarrow I(\mu, T) &= T \int_{-\mu/T}^\infty \frac{(\mu + Tz)^{3/2}}{e^z + 1} dz \\ &= T \int_0^\infty \frac{(\mu + Tz)^{3/2}}{e^z + 1} dz + T \int_0^{\mu/T} \frac{(\mu - Tz)^{3/2}}{e^{-z} + 1} \\ &= T \int_0^\infty \frac{(\mu + Tz)^{3/2}}{e^z + 1} + T \int_0^{\mu/T} (\mu - Tz)^{3/2} dz - T \int_0^{\mu/T} \frac{(\mu - Tz)^{3/2}}{1 + e^z} \end{aligned}$$

Let $x = \mu - Tz$, $dx = -T dz$, $\frac{\mu}{T} \ll 1$:

$$\begin{aligned} I(\mu, T) &= \underbrace{T \int_0^\mu \frac{x^{3/2}}{T} dx}_{\text{0 temp contribution}} + \underbrace{T \int_0^\infty \frac{[(\mu + Tz)^{3/2} - (\mu - Tz)^{3/2}]}{e^z + 1} dz}_{\substack{\text{correction terms} \\ \text{goes to 0 as } T \rightarrow 0 \\ \text{faster than linearly}}} + \mathcal{O}(e^{\mu/T}) \\ &= \frac{2}{5} \mu^{5/2} + T \mu^{3/2} \int_0^\infty \frac{dz}{1 + e^z} \left[\left(1 + \frac{T}{\mu} z\right)^{3/2} - \left(1 - \frac{T}{\mu} z\right)^{3/2} \right] \\ &= \frac{2}{5} \mu^{5/2} + T \mu^{3/2} \int_0^\infty \frac{dz}{1 + e^z} \left[1 + \frac{3}{2} \frac{T}{\mu} z + \mathcal{O}\left(\frac{T^2}{\mu^2}\right) - 1 + \frac{3}{2} \frac{T}{\mu} z \right] \\ &= \frac{2}{5} \mu^{5/2} + 3T^2 \mu^{1/2} \underbrace{\int_0^\infty \frac{z}{1 + e^z} dz}_{\frac{\pi^2}{12}} + \mathcal{O}(T^4) \\ &= \frac{2}{5} \mu^{5/2} + \frac{\pi^2}{4} \mu^{1/2} T^2 + \mathcal{O}(T^4) \end{aligned}$$

$$\begin{aligned} \Rightarrow J &= J_0 - \frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \frac{\pi^2}{4} \mu^{1/2} T^2 + \mathcal{O}(T^4) \\ &= J_0 - \frac{VT^2 m^{3/2}}{6\hbar^3} \sqrt{2\mu} \end{aligned}$$

By §2.2, $\mu = \mathcal{E}_F + \mathcal{O}(T)$,

$$\begin{aligned} &= J_0 - \frac{VT^2 m^{3/2}}{6\hbar^3} \left[\frac{(3\pi^2)^{1/3} \hbar}{\sqrt{2m}} \left(\frac{N}{V} \right)^{1/3} \right] \\ &= J_0 - \frac{T^2 m}{6\hbar^3} (3\pi^2)^{1/3} N \left(\frac{V}{N} \right)^{1/3} \\ &= J_0 - NT^2 \frac{\pi^2}{4} \frac{1}{\mathcal{E}_F} \left[1 + \mathcal{O} \left(\frac{T}{\mu} \right)^2 \right] \end{aligned}$$

Remark 1: We have calculated J at fixed μ (recall that $\mu = \mu(T, N)$)

To get C_v , we need F , not J . But

$$\begin{aligned} &\left. \begin{aligned} dF &= -S dT - p dV + \mu dN \\ dJ &= -S dT - p dV - N d\mu \end{aligned} \right\} (\delta J)_{V,\mu} = (\delta F)_{V,N} \\ &\Rightarrow F = F(T=0) - \frac{NT^2 \pi^2 T}{4\mathcal{E}_F} \\ &\Rightarrow S = \frac{-\partial F}{\partial T} = \frac{Nk_B^2 \pi^2 T}{2\mathcal{E}_F} \quad (k_B \neq 1 \text{ anymore}) \\ &C_v = T \left(\frac{\partial S}{\partial T} \right)_V = \frac{Nk_B \pi^2}{2} \left(\frac{k_B T}{\mathcal{E}_F} \right) + \mathcal{O} \left(\frac{T}{\mathcal{E}_F} \right)^2 \quad (\text{with } g = 2) \quad (\dagger) \end{aligned}$$

Remark 2: Any fermion system of $T \ll T_F$ (eg. electrons in metals at room temperature) has linear T -dependence of specific heat.

2.2.4 Pauli Paramagnetism

By quantum mechanics, for electrons in a magnetic field, the energy depends on the value of the z-component of the spin (Zeeman effect).

$$\mathcal{E}_S = \frac{p^2}{2m} - S\mu_B gB$$

$B =$ magnetic field

$$\mu_B = \frac{e\hbar}{2mc} = \text{bohr magneton}$$

$g = 2$ for electrons

$$S = \pm \frac{1}{2}$$

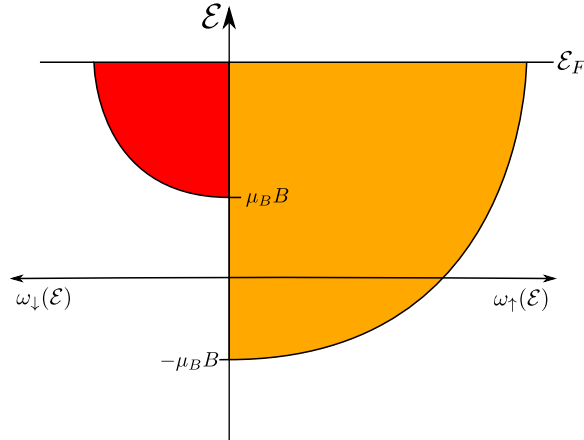
Remark 1: Consider the coupling of B to the electron spin *only*.

Some interesting points:

- Up and Down spins form two different subsystems that can exchange particles.
- $\mu(T = 0) = \mathcal{E}_F$ is independent of S . (Since particles can be exchanged, μ will adjust itself accordingly.)
- There will, however, be different Fermi momenta:

$$\begin{aligned}\frac{p_{F\uparrow}^2}{2m} &= \mathcal{E}_F + \mu_B B & (\text{up spins}) \\ \frac{p_{F\downarrow}^2}{2m} &= \mathcal{E}_F - \mu_B B & (\text{down spin})\end{aligned}$$

Thus there are differing densities of states (See §2.2.1.R5). If we call $\omega_{\uparrow}(\mathcal{E})$ the density of states with up spins, then we have something like: Thus there are more up-spins than



down-spins

$$\begin{aligned}N_{\uparrow} &= \frac{V p_{F\uparrow}^3}{6\pi^2 \hbar^3} = \text{Number of up-spins} \\ N_{\downarrow} &= \frac{V p_{F\downarrow}^3}{6\pi^2 \hbar^3} = \text{Number of down-spins}\end{aligned}$$

$$\begin{aligned}\text{Magnetic Moment} = M &= \mu_B (N_{\uparrow} - N_{\downarrow}) \\ &= \frac{\mu_B V}{6\pi^2 \hbar^3} (2m)^{3/2} \left[(\mathcal{E}_F + \mu_B B)^{3/2} - (\mathcal{E}_F - \mu_B B)^{3/2} \right] \\ &= \frac{\mu_B V}{6\pi^2 \hbar^3} (2m)^{3/2} \mathcal{E}_F^{3/2} \left[\left(1 + \frac{\mu_B B}{\mathcal{E}_F} \right)^{3/2} - \left(1 - \frac{\mu_B B}{\mathcal{E}_F} \right)^{3/2} \right]\end{aligned}$$

Remark 2: $1 \text{ T} = 10 \text{ kG} \approx 1 \text{ K}$

$$\Rightarrow \mu_B B \ll \mathcal{E}_F \quad \text{in metals} \quad (T_F \approx 10^5 \text{ K})$$

One doped semiconductor:

$$T_F \approx 10^2 \text{ K}; \quad B \leq 30 \text{ T}$$

Neutron Stars:

$$T_F = 10^{11} \text{ K}; \quad B = 10^4 - 10^6 \text{ T}$$

Thus $\mu_B B \ll \mathcal{E}_F$ in most all cases.

Remark 3: Thus we have two different regimes, even for $\mu_B B \ll \mathcal{E}_F$:

1. $\mu_B B \ll k_B T \ll \mathcal{E}_F$ – the “weak field regime”

Here the energy spectrum is unchanged by the B fields (that is what we assume).

2. $k_B \ll \mu_B B \ll \mathcal{E}_F$ – the “strong or quantizing field regime”

Here the energy spectrum is drastically changed from the $B = 0$ case. (“Landau Levels” – a completely different physics, see Landau and Lifshitz)

$$\begin{aligned} \Rightarrow M &= \frac{\mu_B V}{6\pi^2 \hbar^3} (2m\mathcal{E}_F)^{3/2} \frac{3\mu_B B}{\mathcal{E}_F} \left[1 + \mathcal{O}\left(\frac{\mu_B B}{\mathcal{E}_F}\right)^2 \right] \\ &= \frac{\mu_B V}{6\pi^2 \hbar^3} (3\pi^2) \hbar^3 \frac{N}{V} \frac{3\mu_B B}{\mathcal{E}_F} \\ &= \frac{3}{2} N \mu_B \left(\frac{\mu_B B}{\mathcal{E}_F} \right) \end{aligned}$$

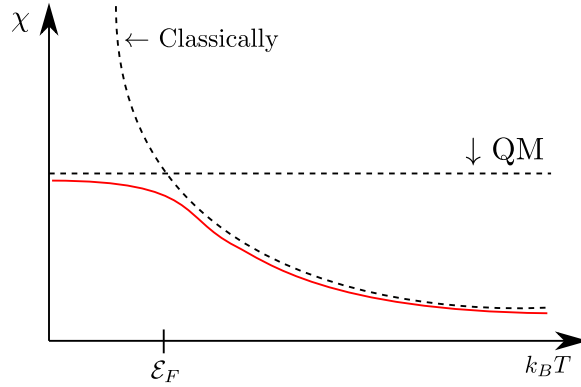
The magnetic susceptibility is thus:

$$\chi = \frac{1}{V} \frac{\partial M}{\partial B}$$

$$\Rightarrow \chi_p = \frac{3}{2} N \frac{\mu_B^2}{\mathcal{E}_F} = \text{Pauli Paramagnetic Susceptibility}$$

Remark 4: Classically, $k_B T \gg \mathcal{E}_F$ and $\chi \sim \frac{\mu_B^2}{T}$. Thus \mathcal{E}_F sets a new energy scale such that

$$\begin{aligned} \chi &\sim \frac{1}{T} \quad \text{for } k_B T \gg \mathcal{E}_F \\ \chi &= \frac{1}{T_F} \quad \text{for } k_B T \ll \mathcal{E}_F \end{aligned}$$



Remark 5: $\chi_p > 0$, as happens with paramagnetism. Note that the orbital angular momentum also couples to the B field, and yields a negative (diamagnetic) contribution to χ .

Remark 6: M can also be obtained from J . (See Hw)

2.3 The Ideal Bose Gas

2.3.1 Bose-Einstein Condensates

Consider an ideal Bose gas. By §1.5.5, we have that

$$\begin{aligned} N &= \sum_k n_\mu(\mathcal{E}_k) = \sum_k \frac{1}{e^{\beta(\mathcal{E}_k - \mu)} - 1} \\ &= \frac{1}{e^{\beta(\mathcal{E}_0 - \mu)} - 1} + \sum_{k \neq 0} \frac{1}{e^{\beta(\mathcal{E}_k - \mu)} - 1} \end{aligned}$$

So $N = N_0 + N' =$ the total number of particles, where

$$\begin{aligned} N_0 &= \frac{1}{e^{-\beta\mu} - 1} = \text{number of particles in the ground state} \\ N' &= \sum_{k \neq 0} \frac{1}{e^{\beta(\mathcal{E}_k - \mu)} - 1} \\ &= \frac{gV m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\mathcal{E}^{1/2}}{e^{\beta(\mathcal{E} - \mu)} - 1} d\mathcal{E} = \text{number of particles in excited states} \end{aligned}$$

Remark 1: We have put $\mathcal{E}_0 = 0$ without loss of generality.

Remark 2: By §2.2.1.R5, $\omega(\mathcal{E}) \sim \mathcal{E}^{1/2}$, and thus in going from the sum to the integral, the ground state gets zero weight.

Remark 3: We can see that $N_0(\mu \rightarrow 0) \rightarrow \infty$. By the Hw, $\mu(T \rightarrow T_0) \rightarrow 0$ with $T_0 > 0$. Thus we can not neglect the number of particles in the ground state, even in the thermodynamic limit.

$$\begin{aligned} N' &= \frac{gV (mk_B T)^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \frac{\sqrt{\pi}}{2} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}}{e^x e^{-\beta\mu} - 1} dx \\ &= gV \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} \cdot I(-\beta\mu) \end{aligned}$$

where

$$I(\alpha) := \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}}{e^x e^\alpha - 1} dx$$

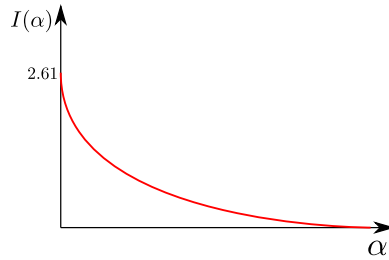
for $\alpha > 0$.

Discussion of $I(\alpha)$:

$$I(0) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}}{e^x - 1} dx = \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}\right) \zeta\left(\frac{3}{2}\right) = \zeta\left(\frac{3}{2}\right) \approx 2.612$$

Since $e^\alpha > 1$, then $I(\alpha)$ is a monotonically decreasing function of α .

$$I(\alpha \rightarrow \infty) = \frac{2}{\sqrt{\pi}} e^{-\alpha} \underbrace{\int_0^\infty x^{1/2} e^{-x} dx}_{\frac{\sqrt{\pi}}{2}} = e^{-\alpha}$$



Thus N' can at most be equal to N'_{max} , and

$$N' \leq N'_{max} = gV \left(\frac{mk_B T}{2\pi \hbar^2} \right)^{3/2} \zeta(3/2)$$

Define T_0 by

$$gV \left(\frac{mk_B T_0}{2\pi \hbar^2} \right)^{3/2} \zeta(3/2) := N$$

$$\Rightarrow k_B T_0 = \frac{A}{g^{2/3}} \frac{\hbar^2}{m} n^{2/3}$$

where

$$A = \frac{2\pi}{[\zeta(3/2)]^{2/3}} = 3.3125$$

Thus, for temperatures less than T_0 , the excited states can not accomodate all of the particles!

Remark 4: See Hw for more.

Proposition: In an ideal Bose gas at $T < T_0$, with

$$k_B T_0 = \frac{A}{g^{2/3}} \frac{\hbar^2}{m} n^{2/3},$$

a finite fraction of particles occupies the ground state, even as $N \rightarrow \infty$.

Remark 5: For the Hw: Show T_0 is the temp where $\mu(T \rightarrow T_0^+) \rightarrow 0^-$.

Remark 6: The accumulation of a finite density of particles in the ground state is called Bose-Einstein condensation.

2.3.2 Chemical Potential and Particle Number for $T < T_0$

By §2.3.1,

$$N_0 = N - N' = \frac{1}{e^{-\beta\mu} - 1}$$

$$\Rightarrow e^{-\beta\mu} = 1 + \frac{1}{N - N'}$$

$$\Rightarrow -\mu = k_B T \ln \left[1 + \frac{1}{N - N'} \right] = k_B T \ln \left[1 + \frac{1}{N - N'_{max}} \right]$$

Remark 1: For a finite number of particles, $\mu(T < T_0)$ assumes a small negative value so that the correct number of $N_0 = N - N'_{max}$ particles are in the ground state.

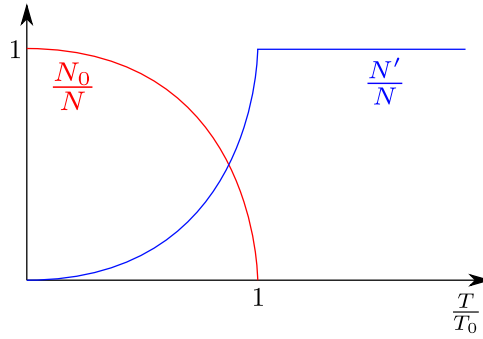
Remark 2: In the thermodynamic limit, $N \rightarrow \infty$, while N'_{max} equals a constant, and thus $\mu(T < T_0) = 0$.

Consider the temperature dependence of N_0 and N' with $T < T_0$:

$$\begin{aligned}
 N' &= gV \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} I(0) \\
 &= \underbrace{gV \left(\frac{mk_B T_0}{2\pi\hbar^2} \right)^{3/2} I(0)}_N \left(\frac{T}{T_0} \right)^{3/2} \\
 &= N \left(\frac{T}{T_0} \right)^{3/2}
 \end{aligned}$$

And thus

$$\frac{N'}{N} = \left(\frac{T}{T_0} \right)^{3/2} \quad \text{and} \quad \frac{N_0}{N} = 1 - \left(\frac{T}{T_0} \right)^{3/2}$$



Remark 3: Entering in n, m for ^4He implies $T_0 = 3.13$ K.

Remark 4: ^4He has a phase transition at $T_\lambda = 2.17$ K. The reason for the difference? ^4He has interactions between particles, unlike the ideal case we have considered here.

Remark 5: Bose-Einstein condensation has been observed in a weakly interacting system.

2.3.3 The Specific Heat of an Ideal Bose Gas

For $T < T_0$, by §3.2 we have that $\mu = 0$. Thus

$$\begin{aligned}
 U &= \sum_k \mathcal{E}_k n_\mu(\mathcal{E}_k) = \frac{gV m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\mathcal{E}^{3/2}}{e^{\beta\mathcal{E}} - 1} d\mathcal{E} \\
 &= \frac{gV (mk_B T)^{3/2} k_B T}{\sqrt{2}\pi^2 \hbar^3} \frac{\sqrt{\pi}}{2} \frac{1}{\sqrt{\pi}} \underbrace{\int_0^\infty \frac{x^{3/2}}{e^x - 1} dx}_{\Gamma(5/2)\zeta(5/2)} \\
 &= gV \underbrace{\left(\frac{mk_B T_0}{2\pi\hbar^2}\right)^{3/2}}_N \zeta(3/2) \frac{1}{\zeta(3/2)} k_B T \left(\frac{T}{T_0}\right)^{3/2} \frac{2}{\sqrt{\pi}} \Gamma(5/2) \zeta(5/2) \\
 &= N \left(\frac{T}{T_0}\right)^{3/2} \frac{k_B T}{\zeta(3/2)} \frac{2}{\sqrt{\pi}} \frac{3}{2} \underbrace{\Gamma(3/2)}_{\frac{\sqrt{\pi}}{2}} \zeta(5/2) \\
 &= N \left(\frac{T}{T_0}\right)^{3/2} k_B T \frac{3}{2} \frac{\zeta(5/2)}{\zeta(3/2)} \\
 &= 0.77 \cdot N k_B T \left(\frac{T}{T_0}\right)^{3/2} \\
 &:= U_0(T) \\
 \Rightarrow C_v(T < T_0) &= \frac{\partial U_0}{\partial T} = \frac{5}{2} \frac{U_0}{T} = \frac{5}{2} \cdot 0.77 \cdot N k_B \left(\frac{T}{T_0}\right)^{3/2}
 \end{aligned}$$

Now, for $T > T_0$, we need to actually know what $\mu(T)$ is!

Lemma:

$$\mu(T \rightarrow T_0^+) = \frac{-2\pi^2 \hbar^6 n^2}{g^2 m^3 (k_B T_0)^2} \left[\left(\frac{T}{T_0}\right)^{3/2} - 1 \right]^2$$

Proof:

$$\begin{aligned}
 N &= \frac{gV m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\mathcal{E}^{1/2}}{e^{\beta(\mathcal{E}-\mu)} - 1} d\mathcal{E} \\
 &= \frac{gV m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \mathcal{E}^{1/2} \left[\frac{1}{e^{\beta(\mathcal{E}-\mu)} - 1} - \frac{1}{e^{\beta\mathcal{E}} - 1} \right] + N''(T)
 \end{aligned}$$

where

$$\begin{aligned}
 N''(T) &= \frac{gV m^{3/2}}{\sqrt{2}\pi^2 \hbar^3} \int_0^\infty \frac{\mathcal{E}^{1/2}}{e^{\beta\mathcal{E}} - 1} d\mathcal{E} \\
 &= N \left(\frac{T}{T_0}\right)^{3/2}
 \end{aligned}$$

Remark 1: For $T < T_0$, N'' would be N' .

Now, assuming $T \rightarrow T_0^+$ and thus that $\mu \rightarrow 0$, the leading contribution to the energy integral comes from $\mathcal{E}_1, \mathcal{E} - \mu \ll 1$.

$$\begin{aligned} \Rightarrow \int_0^\infty \mathcal{E}^{1/2} \left[\frac{1}{e^{\beta(\mathcal{E}-\mu)} - 1} - \frac{1}{e^{\beta\mathcal{E}} - 1} \right] d\mathcal{E} &\approx \int_0^\infty \mathcal{E}^{1/2} \left[\frac{1}{\beta(\mathcal{E}-\mu)} - \frac{1}{\beta\mathcal{E}} \right] d\mathcal{E} \\ &= k_B T \int_0^\infty \mathcal{E}^{1/2} \left[\frac{\mu}{\mathcal{E}(\mathcal{E}-\mu)} \right] d\mathcal{E} \\ &= k_B T \int_0^\infty \frac{\mu}{\sqrt{\mathcal{E}}(\mathcal{E}-\mu)} d\mathcal{E} \end{aligned}$$

Let $x = \mathcal{E} - \mu$

$$\begin{aligned} &= k_B T (-\mu)^{1/2} (-1) \underbrace{\int_0^\infty \frac{1}{\sqrt{x}(x+1)} dx}_\pi \\ &= -\pi k_B T (-\mu)^{1/2} + \mathcal{O}(\mu^{3/2}) \\ \Rightarrow N &= \frac{-gV m^{3/2} \pi}{\sqrt{2} \pi^2 \hbar^3} k_B T \sqrt{-\mu} + \underbrace{N \left(\frac{T}{T_0} \right)^{3/2}}_{N''} \\ \Rightarrow -\mu &= \left(\frac{N}{V} \right)^2 \left[1 - \left(\frac{T}{T_0} \right)^{3/2} \right]^2 \frac{2\pi^4 \hbar^6}{g^2 m^3 \pi^2} \frac{1}{(k_B T)^2} \\ \Rightarrow -\mu &\approx \frac{2\pi^2 \hbar^6 n^2}{g^2 m^3 \underbrace{(k_B T_0)^2}_{\text{to lowest order}}} \left[1 - \left(\frac{T}{T_0} \right)^{3/2} \right]^2 \end{aligned}$$

By §2.1, we know that $J = -pV = -\frac{2}{3}U$.

$$\Rightarrow \frac{\partial U}{\partial \mu} = -\frac{3}{2} \frac{\partial J}{\partial \mu} = \frac{3}{2} N$$

$$\begin{aligned} \Rightarrow U &= U(\mu = 0) + \frac{3}{2} N \mu \\ &= U_0(T) + \frac{3}{2} N \mu(T) \end{aligned}$$

And thus

$$C_v = \frac{\partial U}{\partial T} = \frac{\partial U_0(T)}{\partial T} + \frac{3}{2} N \frac{\partial \mu(T)}{\partial T}$$

Remark 2: We know $\mu(T)$ only to leading order as $T \rightarrow T_0^+$, so let's replace $U_0(T)$ with $U_0(T_0)$ (keeping just the leading order term):

$$\begin{aligned}
 C_v(T \rightarrow T_0^+) &= \left. \frac{\partial U_0}{\partial T} \right|_{T_0} - \frac{3N}{2} \cdot \frac{2\pi^2 \hbar^6 n^2}{g^2 m^3 (k_B T_0)^2} \cdot 2 \left[1 - \left(\frac{T}{T_0} \right)^{3/2} \right] \underbrace{\left(\frac{-3}{2} \right) \left(\frac{T}{T_0} \right)^{1/2}}_{\text{not leading matrix}} \cdot \frac{1}{T_0} \\
 &= C_v(T_0) + \frac{9\pi^2 \hbar^6 n^2}{g^2 m^3} \frac{N k_B}{(k_B T_0)^3} \left[1 - \left(\frac{T}{T_0} \right)^{3/2} \right] \\
 &= C_v(T_0) - N k_b \cdot \frac{9\pi^2 \hbar^6 n^2}{g^2 m^3 (k_B T_0)^3} \left[\left(\frac{T}{T_0} \right)^{3/2} - 1 \right]
 \end{aligned}$$

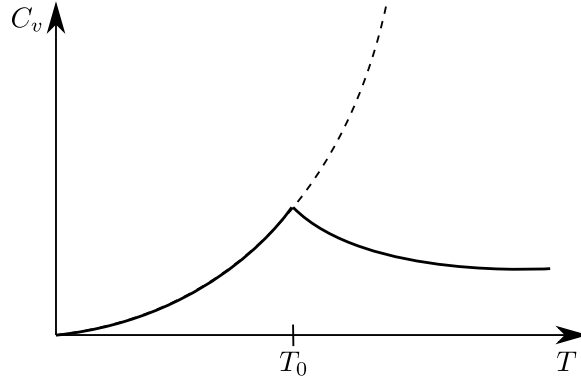


Figure 2.4: Notice the “ λ ” shape, and thus this is called the λ transition.

Remark 3: $C_v(T)$ is continuous, but not differentiable at $T = T_0$, where we have a cusp singularity.

Remark 4: In ^4He , $C_v(T)$ diverges at the λ transition, as interactions lead to a stronger singularity.

2.4 Black Body Radiation

2.4.1 Planck's Law

Consider photons in equilibrium with matter. Photons have spin 1, and thus Bose-Einstein statistics apply.

Remark 1: Photon-photon interactions are *extremely weak*. (mediated by virtual $e^- - e^+$ pairs) Thus some matter is necessary to reach equilibrium.

Remark 2: Photon gas can be considered ideal if the matter is dilute (eg, in a dilute gas or the walls of a cavity whose only role is to absorb and emit photons).

Remark 3: Photon number is *not* fixed.

Proposition 1: A photon gas, in equilibrium with matter, has zero chemical potential.

$$\mu = 0$$

Proof: We want to minimize the free energy with respect to the particle number:

$$0 = \left(\frac{\partial F}{\partial N} \right)_{N,T} = \mu$$

Corollary: The mean number of photons with frequency ω with temp T is:

$$\langle N_\omega \rangle = \frac{1}{e^{\beta \hbar \omega} - 1}$$

Proof: Use a Bose-Einstein distribution with $\mathcal{E}_\omega = \hbar \omega$ and $\mu = 0$.

Proposition 2: The energy contained in the frequency interval $[\omega, \omega + d\omega]$ is given by:

$$dU_\omega = u(\omega) d\omega$$

with the frequency distribution function:

$$u(\omega) = \frac{V \hbar}{\pi^2 c^3} \frac{\omega^2}{e^{\beta \hbar \omega} - 1}$$

This is Planck's Law.

Proof: By §2.1, the momentum distribution is:

$$\rho(p) = \frac{gV}{2\pi^2 \hbar^3} \frac{p^2}{e^{\beta(\mathcal{E}_p - \mu)} - 1}$$

For photons, $\mu = 0$, $\mathcal{E}_p = pc = \hbar \omega$, $g = 2$. ($g \neq 2s + 1$ since the rest mass of photons is 0). Conserving probability:

$$\begin{aligned} \rho(\omega) &= \rho(p) \frac{dp}{d\omega} = \frac{\hbar}{c} \frac{2V}{2\pi^2 \hbar^3} \frac{\hbar^2}{c^2} \frac{\omega^2}{e^{\beta \hbar \omega} - 1} \\ &= \frac{V}{\pi^2 c^3} \frac{\omega^2}{e^{\beta \hbar \omega} - 1} \end{aligned}$$

with $\rho(\omega) d\omega$ being the probability of finding a photon with frequency in the interval $[\omega, \omega + d\omega]$. Each photon carries energy $\hbar\omega$ and thus:

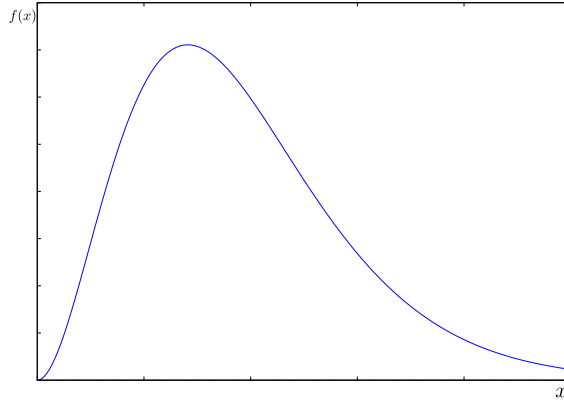
$$u(\omega) = \hbar\omega\rho(\omega) = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$

2.4.2 Discussion of Planck's Law

$$\begin{aligned} u(\omega) &= \frac{V\hbar}{\pi^2 (\beta\hbar c)^3} \frac{(\beta\hbar c)^3}{e^{\beta\hbar\omega} - 1} \\ &= \frac{V (k_B T)^3}{\pi^2 c^3 \hbar^2} f\left(\frac{\hbar\omega}{k_B T}\right) \end{aligned}$$

where

$$f(x) = \frac{x^3}{e^x - 1}$$



Proposition 1: The maximum of the radiation intensity occurs at a frequency:

$$\omega_{max} = 2.82 \frac{k_B T}{\hbar}$$

which is called Wien's Displacement Law.

Proof:

$$\begin{aligned} 0 &= \frac{df}{dx} = \left(\frac{3x^2}{e^x - 1} - \frac{x^3 e^x}{e^x - 1} \right) \Big|_{x_{max}} \\ &= 3 - \frac{x e^x}{e^x - 1} \Big|_{x_{max}} \end{aligned}$$

$$3(e^x - 1) = xe^x \quad \Rightarrow \quad x = 2.822$$

Proposition 2: In the limits of low frequency, $\hbar\omega \ll k_B T$ and high frequency $\hbar\omega \gg k_B T$, Planck's Law simplifies to the Rayleigh-Jeans Law,

$$u(\omega \rightarrow 0) = \frac{V k_B T}{\pi^2 c^3} \omega^2$$

and to Wien's Law,

$$u(\omega \rightarrow \infty) = \frac{V \hbar}{\pi^2 c^3} \omega^3 e^{-\frac{\hbar\omega}{k_B T}}$$

Proof:

$$\begin{aligned} f(x \rightarrow 0) &= x^2 + \mathcal{O}(x^3) \\ f(x \rightarrow \infty) &= x^3 e^{-x} [1 + \mathcal{O}(e^{-x})] \end{aligned}$$

2.5 Relativistic Degenerate Electron Gas

Consider a relativistic electron gas at $T = 0$.

Proposition 1: The internal energy density is given by

$$\frac{U}{V} = \frac{m^4 c^5}{32\pi^2 \hbar^3} [-\xi + \sinh \xi]$$

where

$$\xi = 4 \sinh^{-1} \left(\frac{p_F}{mc} \right)$$

Proof: For a relativistic electron,

$$\mathcal{E}_p = c\sqrt{m^2 c^2 + p^2}$$

And thus

$$\begin{aligned} \langle \mathcal{E}_p \rangle &= \int_0^\infty \mathcal{E}_p \rho(p) dp \\ &= \int_0^\infty c\sqrt{m^2 c^2 + p^2} \frac{gV p^2}{2\pi^2 \hbar^3 (e^{\beta(\mathcal{E}_p - \mu)} + 1)} dp \quad \text{by §2.2.1} \\ &= \frac{cgV}{2\pi^2 \hbar^3} \int_0^{p_F} (m^2 c^2 + p^2)^{1/2} p^2 dp \quad \text{taking } T = 0 \\ &= \frac{cgV}{2\pi^2 \hbar^3} (mc)^4 \int_0^\infty \left(1 + \left(\frac{p}{mc} \right)^2 \right)^{1/2} \left(\frac{p}{mc} \right)^2 d\left(\frac{p}{mc} \right) \\ &= \frac{gV m^4 c^5}{2\pi^2 \hbar^3} \int_0^{p_F/mc} x^2 (1 + x^2)^{1/2} dx \\ &= \frac{gV m^4 c^5}{2\pi^2 \hbar^3} \left[\frac{1}{4} \left(\frac{p_F}{mc} \right) \left(1 + \left(\frac{p_F}{mc} \right)^2 \right)^{1/2} - \frac{1}{8} \left(\frac{p_F}{mc} \right) \left(1 + \left(\frac{p_F}{mc} \right)^2 \right)^{1/2} - \frac{1}{8} \ln \left(\frac{p_F}{mc} + \sqrt{1 + \left(\frac{p_F}{mc} \right)^2} \right) \right] \end{aligned}$$

But

$$\ln(x + \sqrt{1 + x^2}) = \sinh^{-1}(x)$$

And thus

$$\begin{aligned} \ln\left(\frac{p_F}{mc} + \sqrt{1 + \left(\frac{p_F}{mc}\right)^2}\right) &= \sinh^{-1}\left(\frac{p_F}{mc}\right) := \frac{\xi}{4} \\ \Rightarrow \frac{p_F}{mc} &= \sinh\left(\frac{\xi}{4}\right) \end{aligned}$$

$$\begin{aligned} \Rightarrow U &= \frac{gVm^4c^5}{2\pi^2\hbar^3} \left[\frac{1}{4} \sinh\left(\frac{\xi}{4}\right) \cosh^3\left(\frac{\xi}{4}\right) - \frac{1}{8} \sinh\left(\frac{\xi}{4}\right) \cosh\left(\frac{\xi}{4}\right) - \frac{\xi}{32} \right] \\ &= \frac{Vm^4c^5}{32\pi^2\hbar^3} \left[-\xi + 4 \sinh\left(\frac{\xi}{4}\right) \cosh\left(\frac{\xi}{4}\right) \left[-1 + 2 \cosh^2\left(\frac{\xi}{4}\right) \right] \right] \quad \text{with } g = 2 \\ &= \frac{Vm^4c^5}{32\pi^2\hbar^3} \left[-\xi + 4 \sinh\left(\frac{\xi}{4}\right) \cosh\left(\frac{3\xi}{4}\right) + 4 \cosh\left(\frac{\xi}{4}\right) \sinh\left(\frac{3\xi}{4}\right) \right] \\ &= \frac{Vm^4c^5}{32\pi^2\hbar^3} \left[-\xi + \frac{1}{2} \sinh \xi - \frac{1}{2} \sinh\left(\frac{\xi}{2}\right) + \frac{1}{2} \sinh \xi + \frac{1}{2} \sinh\left(\frac{\xi}{2}\right) \right] \\ &= \frac{Vm^4c^5}{32\pi^2\hbar^3} [-\xi + \sinh \xi] \end{aligned}$$

Proposition 2: The equation of state can be written in parametric form as

$$\begin{aligned} n &= \frac{m^3c^3}{3\pi^2\hbar^3} \sinh^3\left(\frac{\xi}{4}\right) \\ p &= \frac{m^4c^5}{32\pi^2\hbar^3} \left[\xi + \frac{1}{3} \sinh \xi + \frac{8}{3} \sinh\left(\frac{\xi}{2}\right) \right] \end{aligned}$$

Proof: By §2.2.2,

$$\begin{aligned} p_F &= (3\pi^2)^{1/3} \hbar n^{1/3} \\ \frac{p_F}{mc} &= \sinh\left(\frac{\xi}{4}\right) = (3\pi^2)^{1/3} \frac{\hbar}{mc} n^{1/3} \\ \Rightarrow n &= \frac{(mc)^3}{3\pi^2\hbar^3} \sinh^3\left(\frac{\xi}{4}\right) \end{aligned}$$

And thus

$$\begin{aligned} p &= \frac{-\partial U}{\partial V} = -\frac{\partial}{\partial V} \left[\frac{Vm^4c^5}{32\pi^2\hbar^3} (-\xi + \sinh \xi) \right] \\ &= \frac{-m^4c^5}{32\pi^2\hbar^3} (-\xi + \sinh \xi) - \frac{Vm^4c^5}{32\pi^2\hbar^3} \left(-\frac{\partial \xi}{\partial V} + \cosh \xi \frac{\partial \xi}{\partial V} \right) \\ &= -\frac{U}{V} + \frac{Vm^4c^5}{32\pi^2\hbar^3} (1 - \cosh \xi) \frac{\partial \xi}{\partial V} \end{aligned}$$

$$\begin{aligned}
\text{but } \frac{\partial \xi}{\partial V} &= \frac{\partial}{\partial V} \left[4 \sinh^{-1} \left(\frac{p_F}{mc} \right) \right] = -\frac{4}{3V} \tanh \left(\frac{\xi}{4} \right) \\
&= -\frac{m^4 c^5}{32 \pi^2 \hbar^3} \left[-\xi + \sinh \xi - \frac{4}{3} \tanh \left(\frac{\xi}{4} \right) (1 - \cosh \xi) \right] \\
&\quad \vdots \\
&= \frac{m^4 c^5}{32 \pi^2 \hbar^3} \left[\xi + \frac{1}{3} \sinh \xi - \frac{8}{3} \sinh \left(\frac{\xi}{2} \right) \right]
\end{aligned}$$

Remark 1: In the non-relativistic limit, $p_F \ll mc$ and thus

$$\begin{aligned}
\frac{p_F}{mc} &= \sinh \left(\frac{\xi}{4} \right) \approx \frac{\xi}{4} \\
\Rightarrow n &= \frac{m^3 c^3}{3 \pi^2 \hbar^3} \left(\frac{p_F}{mc} \right)^3 = \frac{p_F^2}{3 \pi^2 \hbar^3}
\end{aligned}$$

and

$$\begin{aligned}
p &= \frac{m^4 c^5}{32 \pi^2 \hbar^3} \left[\xi + \frac{1}{3} \left(\xi + \frac{\xi^3}{3!} + \frac{\xi^5}{5!} + \dots \right) - \frac{8}{3} \left(\frac{\xi}{2} + \frac{(\xi/2)^3}{3!} + \frac{(\xi/2)^5}{5!} + \dots \right) \right] \\
&= \frac{m^4 c^5}{32 \pi^2 \hbar^3} \left[\frac{1}{4} \frac{1}{5!} \xi^5 + \mathcal{O}(\xi^7) \right] \\
&= \frac{m^4 c^5}{32 \pi^2 \hbar^3} \frac{1}{4} \frac{1}{5!} \left(\frac{4 p_F}{mc} \right)^5 \\
&= \frac{(3\pi)^{2/3} \hbar^2 n^{5/3}}{5m}
\end{aligned}$$

Chapter 3

Introduction to Kinetic Theory

3.1 The Boltzmann Equation

3.1.1 The Fundamental Question of Kinetic Theory

The Model: Consider a gas of particles with no internal degrees of freedom. Collisions are described by classical mechanics, and we will consider only binary collisions.

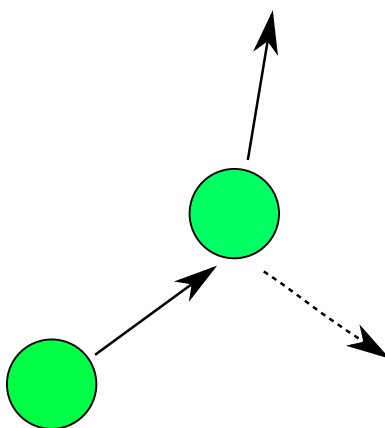


Figure 3.1: In a “dilute gas”, the particles will be rare enough that we can consider only binary collisions (no 2 particles hitting another simultaneously).

Remark 1: The last model assumption restricts us to a dilute gas.

Consider the single particle distribution function from §2.1.5:

$$\begin{aligned} f(\mathbf{v}, \mathbf{x}, t) &\equiv \rho^{(1)}(\mathbf{v}, \mathbf{x}, t) \\ &= \int d\mathbf{v}_2 \dots d\mathbf{v}_n d\mathbf{x}_2 \dots d\mathbf{x}_n \rho(\mathbf{v}, \mathbf{x}, t) \end{aligned}$$

Remark 2: We do not assume equilibrium, and thus f is explicitly time dependent.

The Fundamental Question: What is the equation of motion for f , and what are its solutions?

Remark 3: The answer to this question will reveal how the system approaches equilibrium.

Proposition: The equation of motion for f can be written as a PDE:

$$\left[\frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{x}} + \frac{1}{m} \mathbf{F}_{ext} \cdot \frac{\partial}{\partial \mathbf{v}} \right] f(\mathbf{v}, \mathbf{x}, t) = \mathfrak{C}(f)(\mathbf{v}, \mathbf{x}, t) \quad (\dagger)$$

where

$$\mathfrak{C}(f)(\mathbf{v}, \mathbf{x}, t) = \left(\frac{\partial f(\mathbf{v}, \mathbf{x}, t)}{\partial t} \right)_{collisions}$$

is the time derivative of f due to collisions, and \mathbf{F}_{ext} is the external force, if any (gravity).

Remark 4: (\dagger) is the desired equation of motion for f . Equations of motion for distribution functions are called kinetic equations.

Remark 5: \mathfrak{C} is called the collision operator. It maps f onto some other function $\mathfrak{C}(f)$ in the space of distribution functions.

Remark 6: Once we can determine \mathfrak{C} exactly, the problem is solved exactly by solving the PDE.

Remark 7: Boltzmann's strategy was to classify collision events with respect to the number of particles involved (binary collisions, tertiary collisions, etc). This is effectively a density expansion.

Remark 8: Using \mathfrak{C} for binary collisions gives the Boltzmann equation, which is a low density approximation to (\dagger) .

Proof of Proposition: Assume we have no collisions. then the particle under consideration is a closed subsystem, and thus Liouville's equation holds for $\rho^{(1)} = f$. By

§1.5.1.C4,

$$\begin{aligned}
0 &= \frac{d}{dt} f(\mathbf{v}, \mathbf{x}, t) \\
&= \frac{\partial f}{\partial t} + \frac{\partial f}{\partial \mathbf{x}} \cdot \underbrace{\mathbf{v}}_{\dot{\mathbf{x}}} + \frac{\partial f}{\partial \mathbf{v}} \cdot \underbrace{\frac{1}{m} \mathbf{F}_{ext}}_{\dot{\mathbf{v}}}
\end{aligned}$$

Collisions lead to a non-zero total time derivative:

$$\frac{df}{dt} \neq 0$$

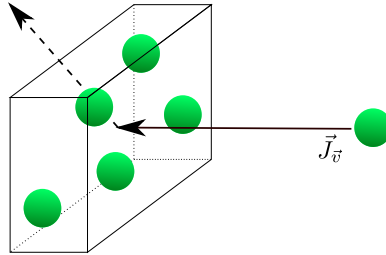
but $\frac{d\rho}{dt} = 0$, which is a statement of conservation of probability.

$$\begin{aligned}
\Rightarrow \frac{df}{dt} &= \left(\frac{df}{dt} \right)_{collisions} = \mathfrak{C}(f) \\
\Rightarrow \mathfrak{C}(f) &= \frac{df}{dt} = \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{x}} + \frac{1}{m} \mathbf{F}_{ext} \cdot \frac{\partial}{\partial \mathbf{v}} \right) f
\end{aligned}$$

3.1.2 The Collision Operator I: Scattering Out Distribution

Let particles with velocities in $[\mathbf{v}, \mathbf{v} + d\mathbf{v}]$ collide with particles with velocities in $[\mathbf{u}, \mathbf{u} + d\mathbf{u}]$. Consider a reference frame moving with velocity \mathbf{u} , and thus the targets are at rest, and hence the scattering particles move with velocity $\mathbf{w} = \mathbf{v} - \mathbf{u}$.

- Cross section for binary scattering: σ
- Number density of incoming particles: $n_{\mathbf{v}} = f(\mathbf{v}, \mathbf{x}, t) d\mathbf{v}$
- Number current density of incoming particles $\mathbf{J}_{\mathbf{v}} = n_{\mathbf{v}} \mathbf{w} = \mathbf{w} f(\mathbf{v}, \mathbf{x}, t) d\mathbf{v}$
- Number of targets in volume $d\mathbf{x}$: $N_{\mathbf{u}} = f(\mathbf{u}, \mathbf{x}, t) d\mathbf{x} d\mathbf{u}$
- Total scattering cross section: $\Sigma = N_{\mathbf{u}} \sigma$
- Number of collisions per unit time: $\Sigma \cdot |\mathbf{J}_{\mathbf{v}}|$



Notice that $d\mathbf{v}$ is infinitesimal, and thus *any* collision will remove the scattering particle from the incoming beam. Thus

$$\begin{aligned}
 \left(\frac{\partial f}{\partial t} \right)_{out} (\mathbf{v}, \mathbf{x}, t) d\mathbf{v} d\mathbf{x} &= -\Sigma \cdot |\mathbf{J}_{\mathbf{v}}| \\
 &= -\sigma f(\mathbf{u}, \mathbf{x}, t) d\mathbf{u} d\mathbf{x} \cdot \mathbf{w} f(\mathbf{v}, \mathbf{x}, t) d\mathbf{v} \\
 &= \text{the number of particles scattered out of the beam} \\
 &\quad \text{per unit time by targets with velocities in } [\mathbf{u}, \mathbf{u} + d\mathbf{u}]
 \end{aligned}$$

Integrating over \mathbf{u} yields:

$$\mathfrak{C}_{out}(f)(\mathbf{v}, \mathbf{x}, t) = -f(\mathbf{v}, \mathbf{x}, t) \int |\mathbf{v} - \mathbf{u}| \sigma f(\mathbf{u}, \mathbf{x}, t) d\mathbf{u}$$

3.1.3 The Collision Operator II: The “Scattering In” Contribution

A colliding pair has characteristics:

$$\left. \begin{array}{ll} \mathbf{u}', \mathbf{v}' & \text{before} \\ \mathbf{u}, \mathbf{v} & \text{after} \end{array} \right\} \text{elastic collision}$$

So by conservation laws:

$$\begin{aligned}
 \mathbf{u} + \mathbf{v} &= \mathbf{u}' + \mathbf{v}' && \text{momentum} \\
 \mathbf{u}^2 + \mathbf{v}^2 &= \mathbf{u}'^2 + \mathbf{v}'^2 && \text{energy} \\
 \Rightarrow (\mathbf{u} + \mathbf{v})^2 &= u^2 + v^2 + 2\mathbf{u} \cdot \mathbf{v} = u'^2 + v'^2 + 2\mathbf{u}' \cdot \mathbf{v}' \\
 &\Rightarrow \mathbf{u} \cdot \mathbf{v} = \mathbf{u}' \cdot \mathbf{v}' \\
 \Rightarrow (\mathbf{u} - \mathbf{v})^2 &= u^2 + v^2 - 2\mathbf{u} \cdot \mathbf{v} = u'^2 + v'^2 - 2\mathbf{u}' \cdot \mathbf{v}' = (\mathbf{u}' - \mathbf{v}')^2 \\
 &\Rightarrow |\mathbf{w}|^2 = |\mathbf{w}'|^2
 \end{aligned} \tag{*}$$

Now let's define the differential cross section as

$$\tilde{\sigma} = \frac{d\sigma}{d\Omega}$$

We will rewrite the “scattering out” term from §3.1.2 using

$$\begin{aligned}
 \sigma &= \int d\sigma = \int \tilde{\sigma} d\Omega' \\
 &\Rightarrow d\mathbf{u} = w^2 dw d\Omega
 \end{aligned} \tag{*}$$

$$\begin{aligned}
\mathfrak{C}_{out}(f)(\mathbf{v}) &= -f(\mathbf{v}) \int d\Omega d\Omega' \int dw w^2 w \tilde{\sigma} f(\mathbf{u}) \\
&= - \int d\Omega d\Omega' \int dw w^3 \tilde{\sigma} f(\mathbf{u}) f(\mathbf{v})
\end{aligned}$$

We can obtain the “scattering in” term from the “scattering out” by interchanging the primed and unprimed (effectively switch before and after) and also changing the sign (since now we are scattering things into the beam, instead of out).

$$\begin{aligned}
\mathfrak{C}_{in}(f)(\mathbf{v}, \mathbf{x}, t) &= + \int d\Omega' d\Omega \int dw' w'^3 \tilde{\sigma} f(\mathbf{u}') f(\mathbf{v}') \\
&= \int d\Omega' d\Omega \int dw w^3 \tilde{\sigma} f(\mathbf{u}') f(\mathbf{v}') \quad \text{by } (\ddagger) \\
&= \int d\Omega' \int d\mathbf{u} w f(\mathbf{u}') f(\mathbf{v}') \tilde{\sigma} \quad \text{by } (\star) \\
\Rightarrow \mathfrak{C}_{in}(f)(\mathbf{v}, \mathbf{x}, t) &= \int d\mathbf{u} \int d\Omega' |\mathbf{v} - \mathbf{u}| \tilde{\sigma} f(\mathbf{u}, \mathbf{x}, t) f(\mathbf{v}, \mathbf{x}, t)
\end{aligned}$$

3.1.4 The Boltzmann Collision Operator

By §3.1.2 and §3.1.3:

$$\begin{aligned}
\mathfrak{C}(f)(\mathbf{v}) &= \mathfrak{C}_{in}(f)(\mathbf{v}) + \mathfrak{C}_{out}(f)(\mathbf{v}) \\
&= \int d\mathbf{u} \int d\Omega' |\mathbf{v} - \mathbf{u}| \tilde{\sigma} [f(\mathbf{v}') f(\mathbf{u}') - f(\mathbf{v}) f(\mathbf{u})]
\end{aligned}$$

Lemma: For any function $F(\mathbf{u}', \mathbf{v}')$:

$$\int d\Omega' |\mathbf{u} - \mathbf{v}| F(\mathbf{u}', \mathbf{v}') = \int d\Omega' \int d\mathbf{v}' \delta(\mathbf{u} + \mathbf{v} - \mathbf{u}' - \mathbf{v}') \cdot \delta(u^2 + v^2 - u'^2 - v'^2) F(\mathbf{u}', \mathbf{v}')$$

Proof: Life is finite... we're skipping it!

Proposition: The Boltzmann collision operator can be written:

$$\mathfrak{C}(f)(\mathbf{v}, \mathbf{x}, t) = \int d\mathbf{u} d\mathbf{u}' d\mathbf{v}' W(\mathbf{u}, \mathbf{v}, \mathbf{u}', \mathbf{v}') \cdot [f(\mathbf{u}', \mathbf{x}, t) f(\mathbf{v}', \mathbf{x}, t) - f(\mathbf{u}, \mathbf{x}, t) f(\mathbf{v}, \mathbf{x}, t)]$$

where

$$W(\mathbf{u}, \mathbf{v}, \mathbf{u}', \mathbf{v}') = \delta(\mathbf{u} + \mathbf{v} - \mathbf{u}' - \mathbf{v}') \delta(u^2 + v^2 - u'^2 - v'^2) \tilde{\sigma}(\chi)$$

with χ being the scattering angle, which will be a complicated function of the velocities.

Remark 1: \mathfrak{C} is a non-linear integral operator.

Remark 2: Since we are considering only binary collisions, then we are “only” dealing with quadratic non-linear functions.

Remark 3: Our derivations ignore correlations between particles before and after collisions.

$$\Rightarrow f(\mathbf{u})f(\mathbf{v}) \quad \text{rather than} \quad \rho^{(2)}(\mathbf{u}, \mathbf{v})$$

Remark 4: In general, $\mathfrak{C}(f) = \mathfrak{C}(\rho^{(1)})$ depends on $\rho^{(2)}$; $\mathfrak{C}(\rho^{(2)})$ depends on $\rho^{(3)}$; etc. This is called a heirarchy of kinetic equations. (BBKGY)

Remark 5: If we assume no correlations, then we have factorization of $\rho^{(2)}$, which closes the hierarchy (though it is still non-linear) and $\rho^{(1)} = f$.

Remark 6: By §2.1.5, $\rho^{(2)}$ factorizes for $N \rightarrow \infty$, and thus the Boltzmann equation is valid (at most) in the thermodynamic limit, and for small densities n . Turns out that the Boltzmann equation is exact for $n \rightarrow 0$ at fixed time t , but *not* for $t \rightarrow \infty$ at fixed small n .

Corollary: The kernel, $W(\mathbf{v}, \mathbf{u}, \mathbf{v}', \mathbf{u}')$, is positive semi-definite, greater than 0, and has the symmetry properties:

$$W(\mathbf{v}, \mathbf{u}, \mathbf{v}', \mathbf{u}') = W(-\mathbf{v}, -\mathbf{u}, -\mathbf{v}', -\mathbf{u}') \quad (1)$$

$$= W(-\mathbf{v}', -\mathbf{u}', -\mathbf{v}, -\mathbf{u}) \quad (2)$$

$$= W(\mathbf{v}', \mathbf{u}', \mathbf{v}, \mathbf{u}) \quad (3)$$

$$= W(\mathbf{u}, \mathbf{v}, \mathbf{u}', \mathbf{v}') \quad (4)$$

Remark 7: The Boltzmann equation has a unique equilibrium solution:

$$f_{eq}(\mathbf{v}, \mathbf{x}, t) \equiv f(\mathbf{v}) = \frac{1}{V} \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T}$$